

On ion exchange equilibria

VI. The heterogeneity of ion exchangers¹By ERIK HÖGFELDT²

With 8 figures in the text

It is a well-known fact that ion exchange resins sometimes are heterogeneous. Samuelson [1a] as well as Calmon [1] and Gregor [2] found that in a typical resin sample swelling properties varied from bead to bead. Lowen *et al.* [3] found that the density varied among the beads and that it was higher the darker the bead. These authors could separate the resin into one light and one dark colored fraction by flotation in concentrated sodium bromide. It was found that the dark fraction had a slightly higher capacity than the light one.

These results, demonstrating differences in swelling, density and capacity of beads from the same batch, make it probable that other quantities also may vary from bead to bead. In the following, some preliminary equilibrium measurements on single resin beads are described where the selectivity is found to be different for different beads. There is also a discussion of a model where an ion exchanger is assumed to contain many different kinds of sites. According to this model bead to bead variations may be due to different proportions of the different kinds of sites. Such models are also used in the fields of gas adsorption equilibria and polyelectrolytes. The treatment below closely follows that used by others for the case of gas adsorption on heterogeneous surfaces.

List of Symbols

$B = K^{-1}$	Empirical constant in the Rothmund-Kornfeld equation.
$f = \frac{\{A^+\}}{\{B^+\}}$	Ratio of the activities of ions A^+ and B^+ in the external water solution.
g	Free energy of reaction.
g', g''	Lowest and highest limits of g .
$\bar{g}(X_{AR})$	Defined analogous with $\bar{k}(X_{AR})$ below.
k, k_i	Equilibrium constants.
$\bar{k}$	Statistical average k .
k', k''	Highest and lowest limit of k .

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$\bar{k}(X_{AR})$	Function giving the average value of k for those of A^+ ions previously unoccupied sites which become occupied when an additional small amount of A^+ ions enter the resin.
K	Empirical constant in the Rothmund-Kornfeld equation.
mM	millimoles per liter.
n_{ARi}, n_{BRi}	Number of moles of ions A^+ and B^+ on the i th kind of site in the resin phase.
n_{AR}, n_{BR}	Total number of moles of ions A^+ and B^+ in the resin phase.
N_i	Number of sites with constant k_i .
$N_a(g), N(g), N(k), N(q)$	Distribution density functions, e.g., $N(g)dg$ gives the number of sites with free energy between g and $g + dg$.
p	Empirical constant in the Rothmund-Kornfeld equation.
q_i, q	Equilibrium constants for the reverse reaction of that defining k_i, k .
q', q''	Lowest and highest limits of q .
$\bar{q}$	Statistical average q .
R	Gas constant.
R^-	Anion framework of resin.
R_i^-	Anion framework of resin for the i th kind of site.
S_0	Total capacity of resin.
dS	Differential of the capacity fraction S and related to the distribution density functions by, e.g., $dS = N(k)dk$, i.e., dS gives the number of sites with constants between k and $k + dk$.
T	Absolute temperature.
u_{ARi}, u_{BRi}	Internal mole fractions. Fractions of the capacity of the i th kind of site occupied by A^+ and B^+ .
$v = \frac{g_{\max} - g}{RT}$	Variable used in transformation of the distribution function $N(g)$.
X_{ARi}, X_{BRi}	External mole fractions. Fractions of total capacity occupied by A^+ and B^+ on the i th kind of site.
X_{AR}, X_{BR}	Stoichiometric mole fractions of A^+ and B^+ in the resin phase.
y_1, y_2	Fractions of total capacity with constants k_1 and k_2 for a two-constant system.
z_A, z_B	Valences of ions A^{z_A+} and B^{z_B+} .
$\delta(g - g_{\max})$	Delta function. Distribution function for a system with only one kind of site.
κ	Equilibrium quotient.
κ', κ''	Limiting values of κ for $X_{BR} = 0$ and $X_{BR} = 1$.
$\varphi(f)$	Isotherm equation.
$\psi = N/N_{\max}$	Variable used in transformation of the distribution function $N(g)$.
ψ_G	Gaussian distribution function.

Experimental

The resins were Dowex 50 of different crosslinkings of sieve fraction 20–50 mesh. They were first saturated with hydrogen ions by flushing a resin column several times, first with 100 mM HNO_3 and thereafter with distilled water. Beads of good spherical shape and without cracks and of size 0.5–1.0 mm in diameter were selected for equilibrium measurements. The capacity of each bead was first determined by saturating the bead with silver ions from a silver nitrate solution containing radioactive silver and comparing the activity of the bead with the activity of a known amount of silver of the same specific activity. The tracer was Ag^{110} , $t_{1/2} = 270$ days, obtained

by neutron bombardment of silver foil in the Brookhaven reactor. The specific activity was such that one ml 10 mM Ag^+ gave a counting rate of ~ 4000 cpm in the deep well scintillation counter used for the measurements. When the capacity had been determined the beads were equilibrated with one ml portions of $\text{AgNO}_3\text{--HNO}_3$ mixtures of ionic strength 100 mM in small vials. The vials were left standing on a laboratory bench overnight (about 12 hours) in a room with a temperature of $22 \pm 2^\circ\text{C}$. It is well known that a temperature variation of this magnitude introduces only a small error in the selectivity coefficient. The ratio solution electrolyte to resin electrolyte was so high ($\sim 50/1$) that the equilibrium composition of the solution was in most cases practically the same as the original one. This was checked by repeating the equilibration with the same $\text{AgNO}_3\text{--HNO}_3$ mixture and obtaining the same composition in the bead. After equilibration the solution was pipetted off, the bead washed several times with distilled water and transferred to a new vial, and the activity determined by counting in the deep-well counter. (It was important to transfer the bead to a new vial since a small amount of activity was sometimes found to be adsorbed on the bakelite cover.) The activity of one ml of the equilibrating $\text{AgNO}_3\text{--HNO}_3$ mixture was also determined so the amount of silver in the bead could be calculated.

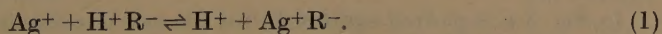
In the beginning some silver balance studies were made. The equilibrium solution and 3 one-ml washings of distilled water were collected in separate vials, and the five vials (resin-bead, solution and washes) were counted in the well counter. Activity balances were $100 \pm 2\%$ with few exceptions. Once good silver balance had been established this technique was abandoned because of the large number of countings to be made for each sample.

A few experiments on reversibility were also made. A bead already equilibrated with, for example, a 30 mM $\text{AgNO}_3\text{--}70$ mM HNO_3 mixture was equilibrated with a 10 mM $\text{AgNO}_3\text{--}90$ mM HNO_3 mixture. The same result as before for this mixture was obtained within the limits $\pm 5\%$.

In order to check that adsorption and Donnan invasion of silver were negligible, saturation experiments were made with three different beads and silver solutions: 1 mM, 10 mM and 100 mM. The same capacity was obtained at all three concentrations within $\pm 5\%$.

For all beads the volume was determined by measuring the diameter of the bead immersed in the equilibrating solution under a microscope, using a calibrated eyepiece. By knowledge of the capacity of the bead the equivalental volume, V_e ml/equivalent, could be calculated.

In Fig. 1 the equivalental volumes, V_e and equilibrium quotient, κ (also called selectivity coefficient), have been plotted against mole fraction of silver in the bead for three different beads from a batch of a 4% DVB resin. κ is defined as the stoichiometric equilibrium constant for the reaction:



As is seen in Fig. 1 there is a large bead to bead variation, several 100%, not only in equivalental volume but also in equilibrium quotient. This variation is much larger than the random spread for each bead which in the worst cases may be as high as $\pm 20\%$ although at least two-thirds of all the data are good to within 2–3%. There is also a correlation between V_e and κ , the larger the equivalental volume the smaller the equilibrium quotient. This is what is to be expected if the degree of crosslinking

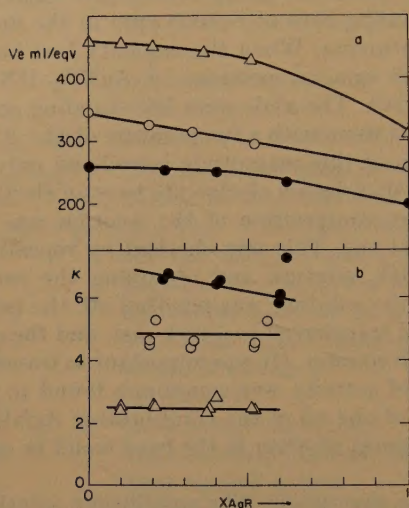


Fig. 1. The equivalental volume, V_e , and equilibrium quotient, κ , plotted against mole fraction of silver in resin, X_{AgR} , for three different beads of a batch from a 4 DVB resin.
○, Bead 1; ●, Bead 2; △ Bead 3.

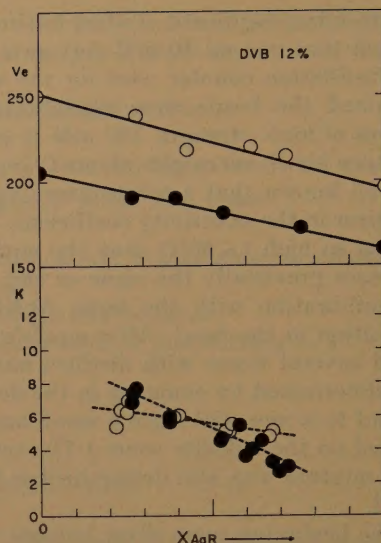


Fig. 2. The equivalental volume, V_e , and equilibrium quotient, κ , plotted against mole fraction of silver in resin, X_{AgR} , for two different beads of a batch of a 12 DVB resin.
○, Bead 1; ●, Bead 2.

varies from bead to bead, and it is very likely that bead to bead variations within the same batch to a first approximation are due to differences in average crosslinking of the beads.

Fig. 2 shows the same quantities for two beads from a resin of 12% DVB. These two beads show the limits of variation in V_e for the beads investigated from that batch. Although the variation is smaller than for the 4% DVB resin the tendency is the same; the highest crosslinked bead seems to have a steeper slope, i.e., is more non-ideal than the lower crosslinked bead.

It deserves also to be mentioned that the straight line relationship in $V_e(X_{AgR})$ observed for all the DVB 12 beads and several of the DVB 4 beads implies a linear water uptake (which is to be expected, since this is what has been found in most cases) and constant partial molar volumes of the two ionic forms. The volume of mixing is thus ideal for the $Ag^+ - H^+$ system on some DVB 4 and all DVB 12 beads. Analogous results have recently been found for gross amounts of beads in the $K^+ - (CH_3)_4N^+$ system [4].

In Fig. 3 κ is plotted against V_e for the two crosslinkings and the mixture 10 mM $AgNO_3$ –90 mM HNO_3 . It is interesting to note how the beads from the DVB 4 resin center around two values, 2.5 and 4.5, corresponding to an average crosslinking of 4 and 8% DVB. No explanation for this behaviour can be offered at present. However, these results indicate with a fair degree of certainty that selectivity may not only vary from batch to batch, but also from bead to bead within the same batch, the variation being due to differences in crosslinking of the beads. Batch to batch variations have already been noted by several workers in the field. They show up as

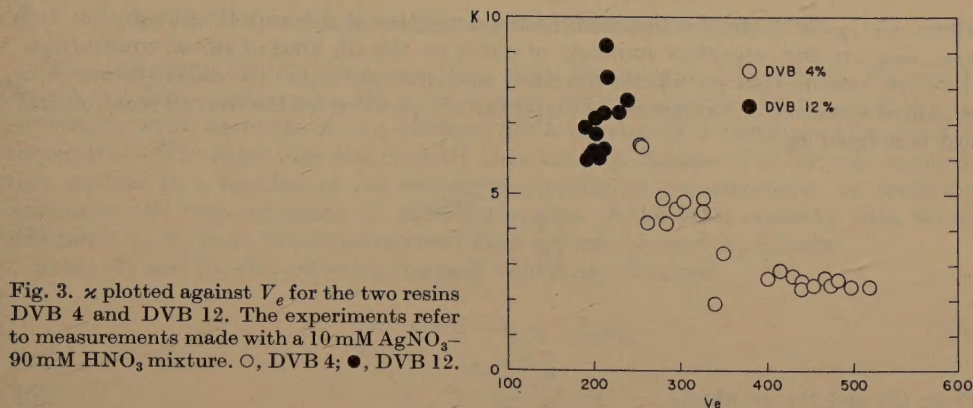


Fig. 3. K plotted against V_e for the two resins DVB 4 and DVB 12. The experiments refer to measurements made with a 10 mM AgNO_3 –90 mM HNO_3 mixture. $\circ$, DVB 4; $\bullet$, DVB 12.

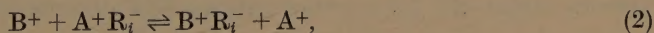
difficulties in reproducing data on what is tacitly assumed to be the same resin. This variation in selectivity is not surprising in view of the known heterogeneity of resins with respect to other properties mentioned in the first paragraph.

Theoretical

The existence of different equilibrium quotients for resin beads from the same batch suggests the possibility of several different types of exchange sites, each with its characteristic equilibrium constant. The sites are distributed differently in different beads, thus giving rise to bead to bead variations. We proceed to investigate theoretically how the experimental equilibrium quotient curve can give information about these different kinds of sites, their relative numbers and the magnitudes of their constants.

The equilibrium quotient as a statistical average of many different constants

The ion exchanger is assumed to contain many kinds of exchange sites, each behaving ideally with its special exchange constant. For the sake of simplicity, we consider exchange between univalent ions on a cation exchanger at such low ionic strength that equivalent exchange occurs (i.e., there is negligible Donnan invasion).¹ For the i th kind of site, we have the following reaction:



where A^+ and B^+ are the two exchanging ions and R_i^- is the anion framework of resin with the i th kind of site.

The equilibrium constant for reaction (2) is defined by:

$$k_i = \frac{\{\text{A}^+\}}{\{\text{B}^+\}} \cdot \frac{n_{\text{BR}_i}}{n_{\text{AR}_i}}, \quad (3)$$

¹ The generalization to multivalent ions is easily made by using the components $(\text{A}_{1/z\text{A}}^{z\text{A}+}) \text{R}^-$, $(\text{B}_{1/z\text{B}}^{z\text{B}+}) \text{R}^-$ and expressing the concentrations in equivalent fractions (cf. Högföldt, Arkiv Kemi 5 (1952) 142, choice E).

where $\{A^+\}$, $\{B^+\}$ are the thermodynamic activities of A^+ and B^+ in solution and n_{AR_i} , n_{BR_i} are the respective numbers of moles on the i th kind of site at equilibrium. Here we assume that for ions in the resin, activities are equal to concentration. The measured quantity, κ , designates the equilibrium quotient for the overall reaction and is defined by:

$$\kappa = \frac{\{A^+\}}{\{B^+\}} \cdot \frac{\sum_{i=1}^n n_{BR_i}}{\sum_{i=1}^n n_{AR_i}}. \quad (4)$$

From (3) and (4) we obtain:

$$\kappa = \frac{\sum_{i=1}^n k_i n_{AR_i}}{\sum_{i=1}^n n_{AR_i}}, \quad (5)$$

which defines κ as the statistical average k for all sites occupied by A^+ .

Introducing the overall mole fractions X_{AR} and X_{BR} where

$$\left. \begin{aligned} X_{AR} &= \frac{\sum_{i=1}^n n_{AR_i}}{S_0}, \\ X_{BR} &= \frac{\sum_{i=1}^n n_{BR_i}}{S_0} \end{aligned} \right\} \quad (6)$$

and S_0 is the total exchange capacity of the resin, equation (5) can be rewritten:

$$\kappa X_{AR} = \sum_{i=1}^n k_i X_{AR_i}, \quad (7)$$

where the external mole fraction X_{AR_i} is defined by

$$X_{AR_i} = \frac{n_{AR_i}}{S_0}. \quad (8)$$

If we eliminate n_{AR_i} instead of n_{BR_i} in (3) the following expression is obtained:

$$\frac{X_{BR}}{\kappa} = \sum_{i=1}^n q_i X_{BR_i}, \quad (9)$$

where X_{BR_i} is defined analogous to X_{AR_i} and $q_i = k_i^{-1}$. To evaluate the sums in (7) and (9), only two limiting cases which are relatively simple to handle will be discussed: (1) two different kinds of sites, and (2) infinite number of different kinds of sites.

1. The ion exchanger is assumed to contain two kinds of sites

This case seems first to have been treated by Damsgaard-Sørensen [5]. He found for the K^+-Na^+ exchange on Permutit G that the exchanger could be described as containing equal amounts of two different kinds of sites with constants 17.2 and 3.5 respectively. The same idea has recently been used by Spinner *et al.* [6] who applied this method to a number of ion exchange equilibrium measurements. In order to determine the two constants k_1 , k_2 and fractions of the total capacity with these constants y_1 , y_2 from the experimental data we can proceed as follows:

From (7) and (9) the following limiting values are obtained:

$$\lim_{X_{BR} \rightarrow 0} \kappa = \kappa' = k_1 y_1 + k_2 y_2, \quad (10)$$

$$\lim_{X_{BR} \rightarrow 1} \frac{1}{\kappa} = \frac{1}{\kappa''} = \frac{y_1}{k_1} + \frac{y_2}{k_2}. \quad (11)$$

The relations (10) and (11) together with the equation

$$y_1 + y_2 = 1 \quad (12)$$

are three relations involving four input quantities. Hence, fixing the value of one of these quantities automatically fixes the other three. In particular, we can use the three equations to compute y_2 , k_1 and k_2 as functions of y_1 , and so compute the curve $\kappa(X_{BR})$ for each value of y_1 .

The expression for $\kappa(X_{BR})$ can be deduced from equations (3)–(9):

$$\kappa = \frac{1}{2 X_{AR}} \left[\kappa' - X_{BR} (k_1 + k_2) + \sqrt{[\kappa' - X_{BR} (k_1 + k_2)]^2 - 4 k_1 k_2 X_{AR} X_{BR}} \right]. \quad (13)$$

The computation is rather simple, as it requires relatively few trial calculations with different y_1 values to fit the data of a $\kappa(X_{BR})$ curve and so obtain best values for k_1 , k_2 and y_1 , y_2 . This method has been applied to the Ag^+-H^+ exchange on Wofatit KS measured by Högfeldt *et al.* [7, 8] which system has been carefully studied over a large range in silver concentration. In Fig. 4 the experimentally determined points are given together with some calculated $\kappa(X_{AgR})$ curves using different values for y_1 . In order to get a good fit over a large concentration range it was necessary to adjust κ'' from 2.8 (the experimentally extrapolated value) to 4.5. The values selected are:

$$\left. \begin{aligned} y_1 &= 0.10, & k_1 &= 224, \\ y_2 &= 0.90, & k_2 &= 4.0. \end{aligned} \right\} \quad (14)$$

As is seen in Fig. 4 there is little difference between $y_1 = 0.08$ and $y_1 = 0.10$ with the adjusted κ'' -value, and the uncertainty in y_1 can be estimated to be ± 0.01 . This choice of constants (14) also gives good agreement with experimental results for low silver concentrations [8] as is seen in Fig. 5, where κ is plotted against $\log X_{AgR}$. The overall agreement between experiment and calculation is rather good considering the large range in X_{AgR} covered (nearly five powers of ten). A better fit could probably

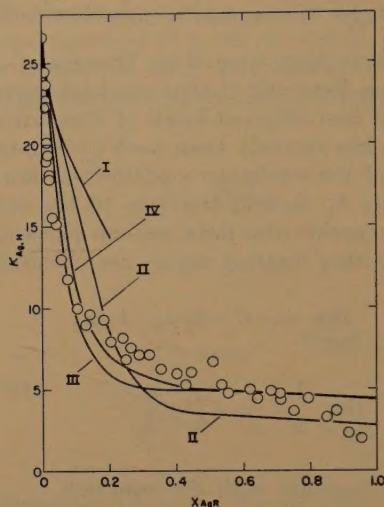


Fig. 4. The equilibrium quotient, κ , plotted against mole fraction of silver, X_{AgR} , for the Ag^+-H^+ exchange on Wofatit KS. $\circ$, Experimental points.

Curve I: Calculated with $y_1 = 0.3$, $y_2 = 0.7$, $k_1 = 82$, $k_2 = 2$ and $\kappa' = 26$, $\kappa'' = 2.8$.

Curve II: Calculated with $y_1 = 0.2$, $y_2 = 0.8$, $k_1 = 122$, $k_2 = 2$ and $\kappa' = 26$, $\kappa'' = 2.8$.

Curve III: Calculated with $y_1 = 0.08$, $y_2 = 0.92$, $k_1 = 278$, $k_2 = 4$ and $\kappa' = 26$, $\kappa'' = 4.5$.

Curve IV: Calculated with $y_1 = 0.10$, $y_2 = 0.90$, $k_1 = 224$, $k_2 = 4$ and $\kappa' = 26$, $\kappa'' = 4.5$.

be obtained by assuming more kinds of sites, but the quantity of computation required increases rapidly with the number of constants assumed. However, the limiting case of an infinite number of constants is tractable, as shown in the following.

2. The ion exchanger is assumed to contain an infinite number of different kinds of sites

1. The function $\bar{k}(X_{AR})$

In this case the sum in equation (7) is replaced by an integral:

$$\kappa X_{AR} = \lim_{\substack{n \rightarrow \infty \\ X_{ARi} \rightarrow 0}} \sum_{i=1}^n k_i X_{ARi} = \lim_{\substack{n \rightarrow \infty \\ u_{ARi} \rightarrow 0}} \sum_{i=1}^n k_i u_{ARi} \frac{N_i}{S_0} = \int_0^1 k u_{AR} dS \quad (15)$$

$$\text{or} \quad \kappa X_{AR} = \int_0^{X_{AR}} \bar{k}(X_{AR}) dX_{AR}, \quad (16)$$

where u_{ARi} , u_{BRi} are the internal mole fractions:

$$u_{ARi} = \frac{n_{ARi}}{N_i}; \quad u_{BRi} = \frac{n_{BRi}}{N_i}. \quad (17)$$

dS gives the differential of the capacity fraction S and from the definition in (15) it is obvious that

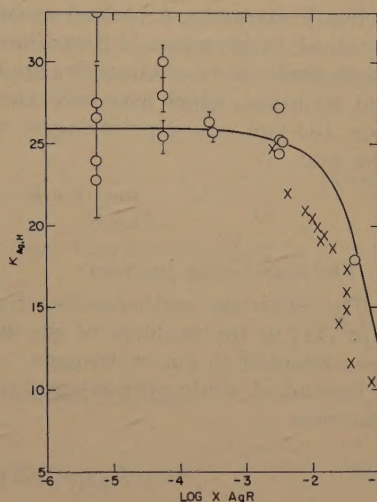


Fig. 5. κ plotted against $\log X_{\text{AgR}}$ for the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS at low silver concentrations. $\circ$, experimental points obtained by radiometric measurements; $\times$, experimental points obtained by emf-titrations; —, curve calculated with $y_1 = 0.10$, $y_2 = 0.90$, $k_1 = 224$, $k_2 = 4$ and $\kappa' = 26$, $\kappa'' = 4.5$.

$$\int_0^1 dS = 1 \quad (18)$$

From (15) and (16), using the definitions of external and internal mole fractions and the calculus of variations, the following expression is obtained (9).

$$\bar{k}(X_{\text{AR}}) = \frac{\int_0^1 k \delta u_{\text{AR}} dS}{\int_0^1 \delta u_{\text{AR}} dS} \quad (19)$$

From equation (19) the physical meaning of the function $\bar{k}(X_{\text{AR}})$ is seen: $\bar{k}(X_{\text{AR}})$ is the average k -value for those previously B^+ -occupied sites which become A^+ -occupied when an additional small amount of A^+ ions enter the resin. By differentiation of (16) we obtain:

$$\bar{k}(X_{\text{AR}}) = \frac{d(\kappa \cdot X_{\text{AR}})}{dX_{\text{AR}}} \quad (20)$$

According to the definition of $\bar{k}(X_{\text{AR}})$ the limiting values of this function will give the range of variation of k .¹ These limits are of interest in the evaluation of the distribution function in the next paragraph.

We take again the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS and treat the data this time under the assumption that there are an infinite number of different kinds of sites. ($\text{A} = \text{H}^+$, $\text{B} = \text{Ag}^+$).

¹ The limits κ' and κ'' do not give the correct limits for the variation in k . It can be shown from (15) and (23) and the analog equations for $\text{B}^+ \text{R}^-$ that $\kappa' = \int_0^\infty k N(k) dk = \bar{k}$ and $\kappa'' = 1/\bar{q}$, where $\bar{q} = \int_0^\infty q N(q) dq$.

Fig. 6 shows $\log \bar{k}$ plotted against X_{AgR} . The points graphed as open circles were obtained by graphical differentiations of the $\kappa \cdot X_{\text{HR}}$ curve. The points graphed as black circles were obtained by analytical differentiation using the Rothmund-Kornfeld equation, which has been shown to fit the experimental data well [10]. As is seen, the two sets of points agree well. The limiting k -values obtained by extrapolation are:

$$\lim_{X_{\text{AgR}} \rightarrow 0} \bar{k} = k' = 420; \quad \lim_{X_{\text{AgR}} \rightarrow 1} \bar{k} = k'' = 2.5. \quad (21 \text{ a, b})$$

2. The distribution function

The following mathematical discussion is an outline of the treatment given by Sips [11] in the problem of gas adsorption on heterogeneous surfaces. Here it has been adapted to ion exchangers.

Instead of solving the integral equation (15) Sips used the analog of the following relations:

$$X_{\text{BR}} = \sum X_{\text{BR}i} = \sum u_{\text{BR}i} \frac{N_i}{S_0} = \int_0^1 u_{\text{BR}} dS. \quad (22)$$

Since the number of sites with constant k is the same as the number of sites with free energy g , dS is related to the three variables g , k and q by the distribution density functions $N(k)$, $N(g)$, $N(q)$ such that

$$dS = -N(k)dk = +N(g)dg = N(q)dq. \quad (23)$$

The minus sign arises from the fact that an increase in g means a decrease in k . From (18) and (23) it is obvious that all the distribution density functions are normalized such that:

$$\int_{g'}^{g''} N(g) dg = \int_{k''}^{k'} N(k) dk = \int_{q'}^{q''} N(q) dq = 1. \quad (24)$$

The transformation from one kind of distribution function to another is easily made using the definition:

$$g = -RT \ln k = RT \ln q. \quad (25)$$

Using equations (3), (17), (23) and (25), equation (22) can be rewritten

$$X_{\text{BR}} = \varphi(f) = RT \int_0^\infty \frac{N(g) dk}{k+f}, \quad (26)$$

where $f = \{A^+\}/\{B^+\}$ equals the quotient of the thermodynamic activities of the ions in the external water solution and $\varphi(f)$ is a mathematical relationship for the isotherm. Following Sips, the k -limits have been set equal to 0 and ∞ . This choice of limits will be subject to discussion later on. By means of a Stieltjes transform, equation (26) solves to:

$$N(g) = \frac{1}{2\pi i} [\varphi(ke^{-\pi i}) - \varphi(ke^{\pi i})]. \quad (27)$$

In order to solve for $N(g)$ we must know $\varphi(f)$. In the literature a number of different empirical equations have been proposed for $\varphi(f)$. Several such equations have recently been discussed in a paper by Högfëldt [10] who found that the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS was well described by the Rothmund-Kornfeld equation:

$$\frac{X_{\text{BR}}}{1 - X_{\text{BR}}} = K f^{-p}, \quad (28 \text{ a})$$

where K and p are empirical constants. Following Sips, this is rearranged to

$$X_{\text{BR}} = \frac{1}{1 + B f^p} = \varphi(f), \quad (28 \text{ b})$$

where $B = K^{-1}$ and inserted in (27) gives the distribution function:

$$N(g) = \frac{B \sin p\pi}{RT\pi} \frac{e^{-pg/RT}}{1 + 2B \cos p\pi e^{-pg/RT} + B^2 e^{-2pg/RT}}. \quad (29)$$

The function has a maximum given by

$$\left. \begin{aligned} N_{\text{max}} &= \frac{1}{2\pi RT} \operatorname{tg} p \frac{\pi}{2}, \\ g_{\text{max}} &= -\frac{1}{p} RT \ln K. \end{aligned} \right\} \quad (30 \text{ a, b})$$

at

The distribution function (29) can be transformed to a simpler form using the following transformations of variables:

$$\begin{aligned} \psi &= \frac{N}{N_{\text{max}}}, \\ v &= \frac{g_{\text{max}} - g}{RT} = \ln \left(\frac{k}{K^{1/p}} \right). \end{aligned} \quad (31 \text{ a, b})$$

Using (31), (29) can be rewritten:

$$\psi = 4 \cos^2 p \frac{\pi}{2} \frac{e^{pv}}{1 + 2 \cos p\pi e^{pv} + e^{2pv}}. \quad (32)$$

Sips found that the distribution function (32) approximated a Gaussian distribution. In order to investigate the validity of this approximation in our case, the distribution function (32) is compared with the following function:

$$\psi = \exp \left[\frac{v^2}{-(2\sqrt{\pi} \cot p \frac{1}{2}\pi)^2} \right]. \quad (33)$$

(32) and (33) are normalized such that:

$$\psi(0) = 1 \text{ and } \int_{-\infty}^{+\infty} \psi dv = 2\pi \cot p \frac{1}{2}\pi \quad (34 \text{ a, b})$$

In Fig. 7 the two curves are plotted using the values $p = 0.75$, $K^{1/p} = 5.50$ found for the $\text{Ag}^+ - \text{H}^+$ system of Wofatit KS [10].

It is seen that the distribution (32) (the full curve) approximates a Gaussian distribution (the dotted curve) reasonably well, and it is to be expected that the isotherm corresponding to a Gaussian distribution must be much like a Rothmund-Kornfeld isotherm. A direct proof of this is difficult as a Gaussian distribution leads to rather intractable integrals, which we have not been able to solve. However, it can be stated that empirically the Rothmund-Kornfeld equation, which has found rather wide application in the field of ion exchange equilibria, corresponds to a nearly Gaussian distribution of sites over free energy of reaction. This result checks a suggestion made by Walton [12, 13] as to the nature of the Rothmund-Kornfeld equation.

The shape of the distribution in Fig. 7 is determined by p . As p approaches unity, i.e., one kind of site, the half width decreases and the distribution becomes a δ function: $\psi(v) = \delta(g - g_{\max})$.¹ In the other limit as p approaches zero, the curve broadens out to $\psi(v) = 1$.

There is another way of calculating an approximation to the distribution function suggested by Roginskii [15]. In the Roginskii approximation the sites are filled up strictly in decreasing order of selectivity, i.e., the sites with highest constants are first occupied followed by the sites next to them going all the way down to the sites with the lowest selectivity. It is obvious that the assumption of Roginskii can only be a good approximation if there is a large spread in selectivity. This has been discussed in a paper by Honig [16], and here it is pointed out that one condition to be fulfilled is that the total spread in molar free energy of reaction is larger than $4.4 RT$, i.e.,

$$g' - g'' = RT \ln \frac{k'}{k''} > 4.4 RT$$

which gives
$$\frac{k'}{k''} > 100. \quad (35)$$

In the Roginskii approximation $\bar{k} = k$ and the distribution density function can simply be obtained by differentiation [14, 15]:

$$N_a(k) = -\frac{1}{d\bar{k}(X_{AR})/dX_{AR}} \quad (36 \text{ a})$$

or
$$N_a(g) = -\frac{1}{dg(X_{AR})/dX_{AR}} \quad (36 \text{ b})$$

where $\bar{g}(X_{AR})$ can be obtained from $\bar{k}(X_{AR})$ using the transformation $g = -RT \ln k$. Since the spread in constants for the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS is larger than 100 (cf. equation (21)) the Roginskii approximation was used, and in Fig. 7

¹ The δ function is defined by $\delta(x) = 0$ for $x \neq 0$, $\int_{-\infty}^{+\infty} \delta(x) dx = 1$. It has the property that for an arbitrary function $N(x)$; $\int N(x) \delta(x) dx = N(0)$ [ref. 14].

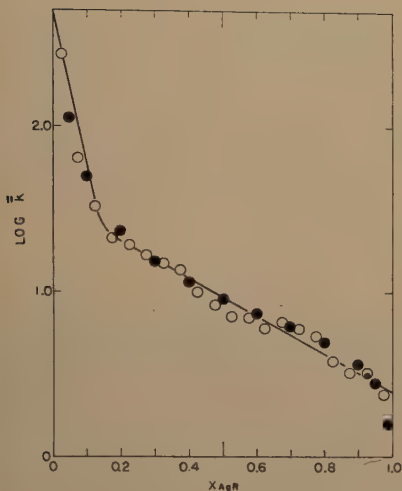


Fig. 6. $\log \bar{k}(X_{\text{AgR}})$ plotted against X_{AgR} for the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS. O, Points obtained by graphical differentiation; ●, points obtained from the Rothmund-Kornfeld equation.

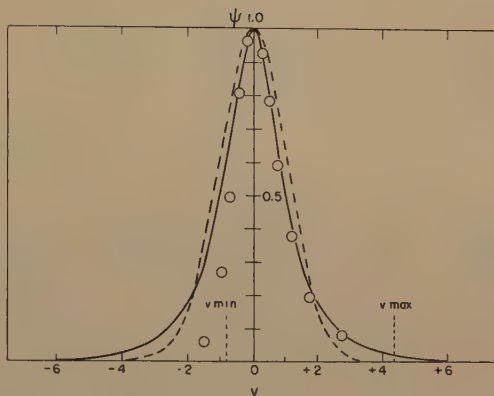


Fig. 7. Distribution function $\psi = N/N_{\text{max}}$ plotted against v for the $\text{Ag}^+ - \text{H}^+$ exchange on Wofatit KS. —, Curve calculated from the Rothmund-Kornfeld equation, (32); ---, curve calculated from a Gaussian distribution, (33); O, points calculated from the approximate distribution function $N_a(g)$, (36b, 31).

the open circles are values calculated from the data in Fig. 6 using (36b) and the variable transformation in equation (31). The agreement between the approximate and exact distribution function (the full curve) is quite good for $v > -0.5$, and for $v > 0$ the two curves are indistinguishable. For $v < -0.5$ the agreement is poor and no symmetrical curve is obtained from the approximation.

3. The integration limits in the integral equation

The integration limits in equation (26) were, for simplicity, chosen as 0 and ∞ . However, the limits obtained by extrapolation from the experimental data were 2.5 and 420 and further discussion is required. In solving the integral equation the Rothmund-Kornfeld equation was used and from this expression the following expression for $\bar{k}(X_{\text{AR}})$ is obtained:

$$\bar{k}(X_{\text{AR}}) = K^{1/p} \left(\frac{X_{\text{AR}}}{1 - X_{\text{AR}}} \right)^{1/p-1} \frac{(1/p - X_{\text{AR}})}{(1 - X_{\text{AR}})} = \frac{\kappa (1/p - X_{\text{AR}})}{(1 - X_{\text{AR}})}. \quad (37)$$

This relation gives the limits 0 and ∞ , and are thus the same as those used by Sips. However, these limits can only be used if the following two conditions are fulfilled:

$$\int_{-\infty}^{v_{\text{min}}} \psi(v) dv \approx 0 \quad \text{and} \quad \int_{v_{\text{max}}}^{\infty} \psi(v) dv \approx 0, \quad (38 \text{ a, b})$$

where $v_{\text{min}} = 2.303 \log (2.5/5.5) = -0.79$; $v_{\text{max}} = 2.303 \log (420/5.5) = 4.39$. In Fig. 7 the v -values corresponding to the limits 2.5 and 420 are marked with dotted vertical

lines. The area under the curve beyond $v_{\max}$ is practically negligible so that condition (38b) is fulfilled with reasonable accuracy. However, this is not the case for the area beyond $v_{\min}$. Either the Rothmund-Kornfeld equation is a poor approximation to the experimental data or the limiting value of k'' too high. There are too few experiments made at high silver concentrations to settle the question. This result shows the importance of making measurements over a very wide concentration range.

Discussion

One fundamental assumption in the model outlined in this paper is that for ions in the exchanger, activities are equal to concentrations. Interactions between adsorbed ions are thus assumed to be negligible, an assumption which might be a poor one, as ion exchangers are known to have a high density of exchange sites.¹ If the non-constancy of κ were due to a distribution of exchange constants only, then only curves with $d\kappa/dX_{\text{BR}} < 0$ (type I [10]) would be possible. This type of curve is indeed the most common one but the existence of other types shows that distribution of exchange constants is not the only effect that needs to be taken into consideration. In particular, the effect of interactions should be studied. On account of the possible existence of interactions, this treatment is not unique, i.e., other assumptions might result in equally good fit of the data. For example, ion pair formation and specific and non-specific interactions between the ions in the resin can also give rise to type I curves. However, the single bead experiments demonstrate that for polystyrene sulfonic acid resins bead to bead variations may exist and heterogeneity can be part of the answer.

It is to be emphasized that the data can be fitted by many different types of distributions. In the present case it has been shown that the analysis of the data with two constants and with an infinite number of constants give fits which are practically the same. Probably any number of constants between those limits will fit the data equally well. This insensitivity of the experimental data to the kind of distribution assumed has already been noticed in the field of gas adsorption [16]. Only extremely careful measurements carried out over a very large concentration range might further limit the number of choices of distributions. The good agreement between the Roginskii approximation and the exact treatment in the continuous constant distribution approach suggests that in cases where the condition $k'/k'' \gg 100$ is fulfilled this method will fast give a distribution curve that cannot be too far from what should be obtained by the elaborate exact treatment.

In the field of ion exchange possible causes of heterogeneity effects have been suggested from time to time. These are of two types. One is chemical heterogeneity [17, 18]. In this model several different kinds of sulfonic acid groups may exist in a presumably homogeneous resin and Bonner [18] has suggested the two kinds of groups shown in Fig. 8 where the second group (II) is due to the introduction of divinylbenzene in the structure. If this picture were correct there should exist a correlation between the amount of DVB introduced in the resin and the fractions of the two kinds of sites.

¹ The author is indebted to Professor O. Samuelson for pointing out that if we start from the Donnan equation, the condition that activity is equal to concentration can be replaced by the less restricted one that the ratio of the activity coefficients of the two ions is constant and independent upon composition for each kind of site.



Fig. 8. Two different kinds of exchange sites due to the incorporation of divinylbenzene in the structure as suggested by Bonner.

In the other model, physical heterogeneity, it is assumed that the density varies from bead to bead and also within the same bead [19, 20]. This density or porosity variation affects the selectivity of the exchanging groups so that each group has its own constant depending upon the local density. It is obvious that the two-constant approach in this paper corresponds to the chemical heterogeneity and the continuous constant distribution approach to the physical heterogeneity, and as a result of this investigation equilibrium data alone cannot decide between the two models. Work is now in progress in this laboratory to attempt to decide which of them is the better approximation.

At last it deserves to be mentioned that the assumption of a probability distribution of exchange constants gives a simple explanation to inversion of selectivity found in several systems [21, 22, 23]. The existence of a number of sites with very high constants requires the existence of an equal number of sites with very small constants. Another explanation to selectivity reversal has been offered by Diamond [24], who suggests changes in hydration of the ions as the cause of the effect. The possibility of selectivity reversal as due to heterogeneity may be kept in mind until a decision can be made in favor of either "explanation."

SYNOPSIS

Preliminary measurements of ion exchange equilibrium quotients on single resin beads show that these quantities vary from bead to bead for the $\text{Ag}^+\text{---H}^+$ exchange on Dowex 50. This heterogeneity effect is studied theoretically and the resolution of the experimental curve in its different components is investigated. Two limiting cases are discussed: (1) the exchanger is regarded as a mixture of two kinds of sites, and (2) an infinite number of kinds of sites with different equilibrium constants. These two models have been applied to data on the $\text{Ag}^+\text{---H}^+$ exchange on Wofatit KS. The analysis using the two-constant model ascribes 10 % of the resin capacity to an equilibrium constant of 224, and the other 90 % to sites with an equilibrium constant of 4. The analysis using the second model results in a continuous distribution of equilibrium constants ranging from 2.5 to 420 with a nearly Gaussian distribution in number of sites over free energies of reaction, which distribution corresponds to the well-known Rothmund-Kornfeld equation for the isotherm. Both methods of analysis fit the data well and the difficulty of obtaining a unique distribution is stressed.

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Uppsala 1959. Almqvist & Wiksells Boktryckeri AB

The interpretation of the h_0 correlation in some acid-catalyzed reactions

By LARS MELANDER and PHILIP C. MYHRE¹

Introduction

The direct proportionality of a reaction rate to the Hammett Acidity Function, h_0 , has generally been explained in terms of a rapid pre-equilibrium of the acid-base type followed by a rate-determining reaction of the conjugate acid:



Furthermore, this kind of dependence has frequently been used as an indication of the existence of the conjugate acid, SH^+ , as a real intermediate. We wish to point out, however, that h_0 proportionality of the reaction rate is not sufficient proof of the existence of the conjugate acid. It can easily be shown by means of the theory of absolute reaction rates that the data concerning the intermediate will cancel from the rate expression. Consequently, purely kinetic measurements will be unable to distinguish between the mechanism shown above and the single step mechanism:



The same will be true for any type of "rapid pre-equilibrium", provided, of course, that the equilibrium lies far to the left.

The statements above do not imply that pre-equilibria in acid-catalyzed reactions never occur but only that they will have to be elucidated by independent methods. It seems that Long and Paul in their recent review have expressed [1a] mainly the same opinion although they have not acknowledged the impossibility of distinguishing between the two mechanisms on the basis of kinetics alone.

It is interesting to note that Zucker and Hammett in their well-known paper of 1939 [2] wrote that the h_0 correlation "— — — is simply explained in terms of the transition state theory of reaction velocity if the equilibrium between reactants and activated complex, whose position determines the rate of reaction, is or approximates an ionization equilibrium of the correct charge type." In several cases this principle seems to have been overlooked.

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Kinetic identity of one-step and two-step mechanisms

The rate-determining expression for the reaction mechanism shown in (1) and (2) is generally written

$$\text{rate} = \frac{k}{K_{\text{SH}^+}} [\text{S}] [\text{H}^+] \frac{f_{\text{S}} f_{\text{H}^+}}{f^\ddagger} \quad (4)$$

where k is the specific rate constant of the slow step, K_{SH^+} is the acid ionization constant of SH^+ , $[\]$ means concentration and f means activity coefficient. The sign ‡ refers to the transition state.

The equilibrium constant, $1/K_{\text{SH}^+}$, for the equilibrium shown in (1) may be written

$$1/K_{\text{SH}^+} = e^{-\Delta F_1/RT} \quad (5)$$

where ΔF_1 is the standard free energy change in this same equilibrium reaction



According to the theory of absolute reaction rates [3] the rate constant for the slow step is

$$k = \kappa \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \quad (7)$$

where $\Delta F^\ddagger$ is the standard free energy of activation, i.e. the free energy change in the activation equilibrium of (2):



The other symbols have their ordinary meaning, κ being the transmission coefficient.

Combining equations (5) and (7) gives

$$\frac{k}{K_{\text{SH}^+}} = \kappa \frac{kT}{h} e^{-\frac{(\Delta F^\ddagger + \Delta F_1)}{RT}} \quad (9)$$

On taking the sum of the free energy changes, $\Delta F^\ddagger$ and ΔF_1 , the free energy of SH^+ cancels, and the sum is equal to the free energy of activation of the single step mechanism (3) assuming the transition states of (2) and (3) are identical. Thus, it is evident that the two alternative mechanisms will lead to the same kinetic expression which contains no information about the postulated intermediate.

Influence of solvation of the proton

If water or some other proton solvating species enters the transition state, the kinetics may change their form. Pure solvation of the proton, however, does not affect the kinetics. Suppose m molecules of water enter the transition state and that $m+n$ molecules of water initially solvate the proton. The activation equilibrium will then be written



Consequently the rate expression is [3a]^{1, 2}

$$\text{rate} = \kappa \frac{kT}{h} K^{\ddagger} \frac{[S][H^+ (H_2O)_{m+n}]}{[H_2O]^n} \cdot \frac{f_S f_{H^+ (H_2O)_{m+n}}}{f^{\ddagger} f_{H_2O}^n} \quad (11)$$

There exists a solvation equilibrium of the type

$$K_s = \frac{[H^+ (H_2O)_{m+n}]}{[H^+][H_2O]^{m+n}} \cdot \frac{f_{H^+ (H_2O)_{m+n}}}{f_{H^+}^{m+n} f_{H_2O}^m} \quad (12)$$

Combining equations (11) and (12) we obtain

$$\text{rate} = \kappa \frac{kT}{h} K^{\ddagger} K_s [S][H^+][H_2O]^m \frac{f_S f_{H^+} f_{H_2O}^m}{f^{\ddagger}} \quad (13)$$

It is obvious that the number n will not affect the concentration factors in the rate expression, and hence the number of proton solvating molecules is irrelevant for the kinetic form. The constant K_s , however, depends on $m+n$ and accounts for the free energy of solvation of the proton.

If $m=0$, as in the mechanisms shown on one hand in (1) and (2) and on the other in (3), the rate expression reduces to equation (14) which is equivalent to the rate equation (4).

$$\text{rate} = \kappa \frac{kT}{h} K^{\ddagger} K'_s [S][H^+] \frac{f_S f_{H^+}}{f^{\ddagger}} \quad (14)$$

This expression gives the familiar relationship between the rate and h_0 upon substitution of $h_0 f_{BH^+}/f_B$ for $[H^+]/f_{H^+}$

$$\text{rate} = \kappa \frac{kT}{h} K^{\ddagger} K'_s h_0 [S] \frac{f_S f_{BH^+}}{f^{\ddagger} f_B} \quad (15)$$

It is usually assumed that the activity coefficient ratio $f_S f_{BH^+}/f^{\ddagger} f_B$ is constant.

If $m=1$ the rate expression (13) may be written

$$\text{rate} = \kappa \frac{kT}{h} K^{\ddagger} K''_s [S][H_3O^+] \frac{f_S f_{H_3O^+}}{f^{\ddagger}} \quad (16)$$

where K''_s is composed of two equilibrium constants accounting for the free energy of solvation of the proton in H_3O^+ as well as in possible higher solvation complexes. Owing to similarity between $S + H_3O^+$ and the present transition state, the activity coefficient ratio might be fairly constant as a first approximation.

¹ By-products in the formation of the transition state should be accounted for in the denominator of the rate expression, a fact that seems to have been frequently overlooked. If in some case the conjugate base, A_i^- , of some acid, HA_i , plays the role of such a by-product, $f_{A_i^-} [A_i^-]$ should be placed in the denominator.

² $K^{\ddagger}$ denotes here the thermodynamic equilibrium constant.

Some experimental data support this view. Thus the relation between the kinetics and the number of solvent molecules included in the transition state is in accord with the one of Zucker and Hammett [2].

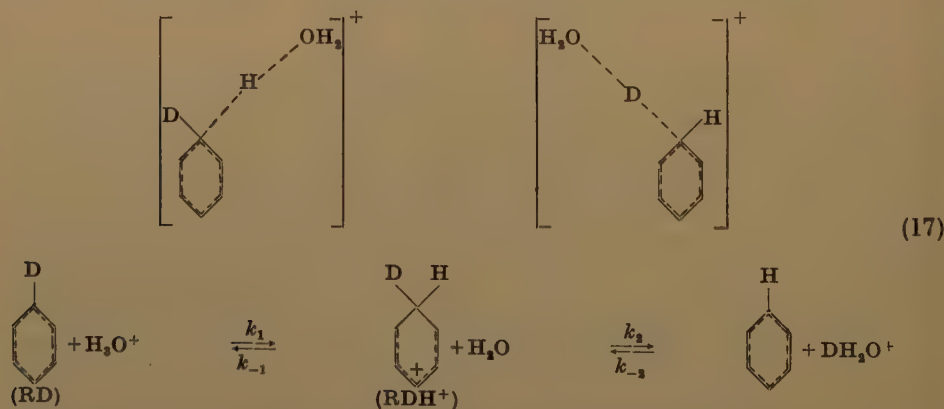
As pointed out by Long and Paul [1 b], there are probably intermediate examples. In some cases it might be more or less a matter of choice if one molecule of water is to be included in the transition state or considered as part of the solvent. In such cases the activity coefficient ratios of equations (15) and (16) will be far from constant with changing medium.

Aromatic electrophilic hydrogen exchange

The assumption of a rapid pre-equilibrium seems quite natural when atoms with lone and not too tightly held electron pairs are involved in the reaction, e.g. oxygen and nitrogen. However, it seems less natural with unsaturated carbon compounds where the electron pairs are delocalized over at least two carbon atoms. Similar views have been expressed by Long and Paul [1 a].

In order to explain the approximate proportionality between the observed rate of aromatic hydrogen exchange and h_0 , Gold and Satchell [4] proposed the idea of a rapid pre-equilibrium between the aromatic molecule and a proton on one hand and a " π -complex" on the other. The rate-determining step involved an intramolecular rearrangement of the latter. In view of the discussion above, it can be seen that a π -complex is neither required nor proved by the kinetics, and that the dependence on h_0 may indicate that basic species play a minor role in the transition state.¹ In order to illustrate these principles, the following two rate expressions with and without a water molecule in the transition state may be derived. The σ -complex intermediate written in the schemes below is in agreement with the commonly accepted picture of electrophilic aromatic substitution. The transition states are pictured above the arrows.

Case I. One molecule of water takes part in the transition state.



¹ Schubert and coworkers [5] have shown that more complicated reactions may give proportionality to h_0 over considerable ranges of acidity. Thus, the h_0 correlation is not a sufficient criterion for the assignment of mechanism.

Assuming the steady-state approximation to be valid and neglecting the reverse reaction, we obtain the following;

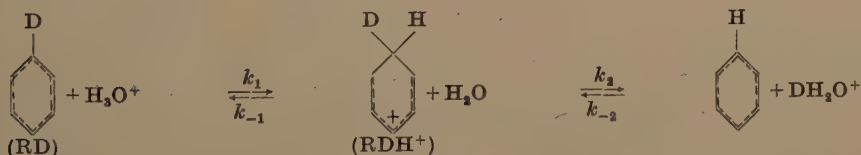
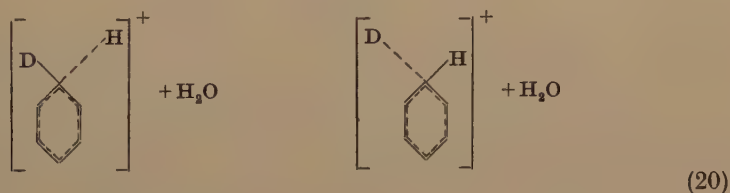
$$\begin{aligned} \frac{d[\text{RDH}^+]}{dt} = k_1[\text{RD}][\text{H}_3\text{O}^+] \frac{f_{\text{RD}} f_{\text{H}_3\text{O}^+}}{f^\ddagger} - k_{-1}[\text{RDH}^+][\text{H}_2\text{O}] \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger} - \\ - k_2[\text{RDH}^+][\text{H}_2\text{O}] \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger} = 0 \quad (18) \end{aligned}$$

where the transition states for steps 1 and 2 are assumed to have the same activity coefficient.

$$\text{rate} = k_2[\text{RDH}^+][\text{H}_2\text{O}] \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{RD}][\text{H}_3\text{O}^+] \frac{f_{\text{RD}} f_{\text{H}_3\text{O}^+}}{f^\ddagger} \quad (19)$$

Assuming the activity coefficient ratio is constant, one would expect proportionality of the rate to $[\text{H}_3\text{O}^+]$. This is not in agreement with experimental results [4].

Case II. Water does not take part in the transition state.



$$\begin{aligned} \frac{d[\text{RDH}^+]}{dt} = k_1 \frac{[\text{RD}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} \cdot \frac{f_{\text{RD}} f_{\text{H}_3\text{O}^+}}{f^\ddagger f_{\text{H}_2\text{O}}} - k_{-1} \frac{[\text{RDH}^+][\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} \cdot \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger f_{\text{H}_2\text{O}}} - \\ - k_2 \frac{[\text{RDH}^+][\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} \cdot \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger f_{\text{H}_2\text{O}}} = 0 \quad (21) \end{aligned}$$

As above, the two transition states in the present mechanism are assumed to have the same activity coefficient.

$$\text{rate} = k_2 \frac{[\text{RDH}^+][\text{H}_2\text{O}]}{[\text{H}_2\text{O}]} \cdot \frac{f_{\text{RDH}^+} f_{\text{H}_2\text{O}}}{f^\ddagger f_{\text{H}_2\text{O}}} = \frac{k_1 k_2}{k_{-1} + k_2} \cdot \frac{[\text{RD}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} \cdot \frac{f_{\text{RD}} f_{\text{H}_3\text{O}^+}}{f^\ddagger f_{\text{H}_2\text{O}}} \quad (22)$$

$$\text{Since} \quad K_s = \frac{[\text{H}_3\text{O}^+]}{[\text{H}^+][\text{H}_2\text{O}]} \cdot \frac{f_{\text{H}_3\text{O}^+}}{f_{\text{H}^+} f_{\text{H}_2\text{O}}} \quad (23)$$

$$\text{rate} = \frac{k_1 k_2}{k_{-1} + k_2} K_s [\text{RD}] [\text{H}^+] \frac{f_{\text{H}^+} f_{\text{RD}}}{f^\ddagger} = \frac{k_1 k_2 K_s}{k_{-1} + k_2} [\text{RD}] h_0 \frac{f_{\text{RD}} f_{\text{BH}^+}}{f^\ddagger f_{\text{B}}} \quad (24)$$

If the activity coefficient ratio is constant the specific rate will be proportional to h_0 . It appears that the results of Gold and Satchell [4] and the recent ones of Satchell [6] approach Case II.

The work of Brown and Brady [7] indicates that "outer" or " π " complex formation occurs between aromatic nuclei and acidic species. According to Glasstone, Laidler and Eyring [3 b] "— — — the presence of intermediate states is inconsequential except in so far as such a state contains an appreciable fraction of the total molecules, which makes them really part of the initial state. It is possible for systems to pass over the highest barrier without necessarily having been through the intermediate states." Since it is possible that there are several minima in the potential energy curve corresponding to various weak interactions prior to the transition state, it is hard to know what to include in the mechanism. Consequently, it seems prudent and most practical to exclude all such intermediates from a proposed mechanism based on kinetic data which are not demanded by the kinetics.

Hydration of olefins

Taft and coworkers [8] have made an extensive study of the hydration of simple olefins in aqueous acid. They find proportionality between the observed rate and h_0 . On the basis of this evidence they postulated that the first step in the hydration mechanism was a rapid proton transfer to the π -bond of the olefin followed by the rate-determining migration of the proton to one of the carbon atoms forming a "free" carbonium ion. The arguments advanced above make it clear that the kinetic evidence alone does not establish the existence of the π -complex intermediate but only serves to demonstrate that the transition state leading to the carbonium ion does not contain a tightly bonded water molecule.

The correlation of the rate of hydration in varying concentrations of deuterium oxide with the theoretical predictions of Nelson and Butler [9] may or may not justify the inclusion of the π -complex in the reaction mechanism. If the transition state is in equilibrium with the reactants as is generally supposed, it would appear that the Nelson-Butler correlation would be equally applicable to reactions which proceed via a rapid pre-equilibrium in the classical sense and reactions which do not.

SUMMARY

It has been shown that the correlation of the rate of an acid-catalyzed reaction to the h_0 function does not necessarily imply that a rapid pre-equilibrium precedes the rate-determining step.

The aromatic hydrogen exchange reaction and the hydration of olefins have been interpreted in terms of this principle. It can be concluded that the presence of π -complexes as an intermediate in either of the above reactions is neither required nor proved by the kinetics.

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Formation and structure of mercuric peroxides

By NILS-GÖSTA VANNERBERG

With 2 figures in the text

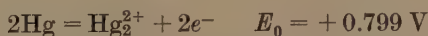
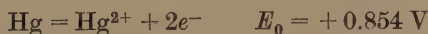
Introduction

Mercurous peroxide, Hg_2O_2 , is reported to have been prepared by von Antropoff (1). By treating metallic mercury with hydrogen peroxide solution, he obtained a black, easily decomposable compound, the colour of which changed to red in a couple of hours. Since no analysis is reported, however, it is doubtful, whether the compound obtained actually was mercurous peroxide.

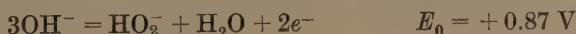
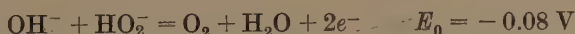
The mercuric peroxide, HgO_2 , was prepared by von Antropoff (2, 3) and Pellini (4) by treating mercuric oxide or mercuric oxynitrate with 30 % hydrogen peroxide solution. Pellini had also prepared the compound from a solution of mercuric chloride and hydrogen peroxide in alcohol (4). According to these authors, mercuric peroxide is a red instable compound, which detonates when struck or heated.

Generally, peroxides of such metals, which can easily change oxidation states, do not exist. The reason for this is that the peroxide group has both oxidizing and reducing properties, and can therefore oxidize the metallic ion from its lower to its higher oxidation state under evolution of oxygen and then reduce the metallic ion from a higher oxidation state to a lower.

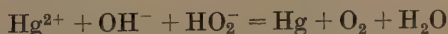
The normal potential for the oxidation of metallic mercury to mercuric or mercurous ion are (5)



The following oxidation-reduction couples involving the hydroperoxide ion have the potentials



The potential for the reaction



is then +0.93 V and for the reaction



the potential becomes +0.02 V.

Similar values are obtained if it is assumed that Hg_2^{2+} takes part in the reactions. It is obvious that if we want to prepare mercuric peroxide from a solution, the concentration of mercuric ion and hydroxyl ion in this solution must be as low as possible; otherwise the mercuric ions will oxidize the hydroperoxide ions to oxygen. It is therefore impossible to precipitate mercuric peroxide from an alkaline solution of mercuric nitrate. In this case mercuric ions react violently with hydrogen peroxide ions to form oxygen and metallic mercury. If, on the other hand, mercuric oxide is treated with hydrogen peroxide solution at low temperatures, the concentration of mercuric ions will be low because of the low solubility of mercuric oxide and peroxide. The same reason will cause a low concentration of hydroxide and hydroperoxide ions. Accordingly, this can be a useful method to prepare mercuric peroxides.

Experimental

In all cases the peroxide samples were obtained by treating yellow mercuric oxide with hydrogen peroxide solutions of various strength and at various temperatures. To determine the peroxide content, a weighed sample was suspended in a cold sulphuric acid solution and titrated with potassium permanganate. The mercury content was determined as mercuric sulphide. The sample was dissolved in diluted hydrochloric acid, and the solution was boiled to decompose all hydrogen peroxide. Hydrogen sulphide was then passed through the solution and the mercuric sulphide formed was dried and weighed.

Table 1.

Compound	Colour	% Hg obs.	% Hg calc.	% O_2 obs.	% O_2 calc.
$\alpha\text{-HgO}_2$	yellow	85.7	86.2	13.3	13.8
$\beta\text{-HgO}_2$	red-yellow	86.4	86.2	13.3	13.8

If yellow mercuric oxide is treated with 20 % hydrogen peroxide at the melting point of the solution, which is about -15°C , a yellow peroxide is formed. According to the analysis (Table 1) its formula is found to be HgO_2 . This peroxide is here called α -mercuric peroxide; it explodes if heated or otherwise carelessly handled.

β -Mercuric peroxide can be prepared if yellow mercuric oxide is treated at the lowest possible temperature with a strong hydrogen peroxide solution. The strength of the solution must be higher than 30 % hydrogen peroxide. The analysis shows the same formula as for the α -compound (Table 1). β -Mercuric peroxide is a red-yellow instable compound. It seems, however, to be somewhat less sensitive to blow than the α -mercuric peroxide.

Crystallographical investigation

From all preparations X-ray photographs were taken with the aid of Guinier powder cameras using Cu $K\alpha$ radiation. The powder pattern of α -mercuric peroxide was very simple and of good quality. It could be indexed on the assumption of a cubic elementary cell with $a = 4.74 \text{ \AA}$. This indicates three formula units in the

Table 2.

$$\alpha = 4.736 \pm 0.005, \alpha = 90^\circ.$$

hkl	$\sin^2 \theta_{\text{obs}} \cdot 10^4$	$\sin^2 \theta_{\text{calc}} \cdot 10^4$	I
110	527	530	vst
111	795	795	st
210	1324	1325	st
220	2120	2120	st-
300.221	2381	2385	w
311	2916	2915	w
222	3174	3180	m
321	3716	3710	vw
410.322	4510	4505	w

elementary cell. However, an optical investigation showed a small birefringence; thus it is probable that this structure has rhombohedral symmetry with $a = 4.74 \text{ \AA}$ and α very close to 90° . The structure is not yet completely solved.

The Guinier powder pattern of β -mercuric peroxide could be interpreted on the assumption of an orthorhombic elementary cell with

$$a = 6.080 \pm 0.010 \text{ \AA}$$

$$b = 6.010 \pm 0.010 \text{ \AA}$$

$$c = 4.800 \pm 0.010 \text{ \AA}$$

The observed and calculated $\sin^2 \theta$ values are given in Table 3.

Table 3.

$$a = 6.080 \pm 0.005, b = 6.010 \pm 0.005, c = 4.800 \pm 0.005.$$

hkl	$\sin^2 \theta_{\text{obs}} \cdot 10^4$	$\sin^2 \theta_{\text{calc}} \cdot 10^4$	I
111	586	584	vst
200	643	643	st
020	658	658	st
002	1033	1033	st
220	1302	1301	m
202	1674	1676	m
022	1690	1690	m
311	1869	1870	m
131	1900	1900	m
222	2336	2334	m
113	2647	2649	m
331	3181	3179	w
420 }	3254	3230	vw
240 }		3272	
402	3600	3605	vvw
042	3666	3666	vvw
313 }	3953	3935	w
133 }		3965	
004	4127	4130	vvw
422	4262	4263	w
242	4304	4309	w

Table 4.

<i>h k l</i>	<i>I</i> ₀	<i>I</i> _c	<i>F</i> ₀	<i>F</i> _c
1 1 1	113	140	210	236
2 0 0	50	49	300	292
0 2 0	50	49	300	291
0 0 2	22	22	260	255
2 2 0	24	29	220	239
2 0 2	16	17	210	216
0 2 2	16	17	210	215
3 1 1	25	25	200	195
1 3 1	25	25	200	195
2 2 2	17	17	190	186
4 0 0	23	3	170	170
0 4 0		3	170	169
1 1 3		13	200	174
3 3 1	14	8	150	160
4 2 0		4	150	152
2 4 0		4	150	151
4 0 2	4	2	130	142
0 4 2		2	130	141
3 1 3		5	130	135
1 3 3	10	5	130	135
0 0 4	1	1	110	121
4 2 2	6	4	110	127
2 4 2		4	110	127
5 1 1		4	120	131
1 5 1	7	4	120	131
2 0 4	4	2	130	113
0 2 4		2	130	113
4 4 0		1	100	110
3 3 3	3	2	100	109

As mercuric peroxide is a very unstable compound, it is very difficult to determine its density, but the number of formula units in the elementary cell can be calculated in another way.

The volume of the elementary cell is 144 Å³. The corresponding value for strontium peroxide SrO₂ is 165 Å³ (6). This cell holds four formula units. As the ions Sr²⁺ and Hg²⁺ have nearly the same radii it is probable that there are four formula units in the elementary cell of β-HgO₂, too.

Besides Guinier photographs, the powder pattern was recorded with a Philips X-ray diffraction unit. From the intensities it seemed probable that the structure was pseudotetragonal. Pairs of reflexions of the type *hkl* and *khl* have the same intensities. Sometimes such pairs of reflexions were not resolved. In these cases it was assumed that the total intensity could be shared equally between the two reflexions. The intensities were corrected for Lorentz and polarization factors. The calculated structure factors were multiplied by $e^{-B(\sin^2\theta/\lambda^2)}$ where *B* is 2.6 Å².

All reflexions with mixed indices are absent, which points to a face-centered cell. However, it is plausible that only the mercury atoms form a face-centered lattice, since it is impossible to record reflexions dependent upon the oxygen atoms only. The possible space groups are then *Fmmm*, *F222*, *Fmm2* and *Pccn* or *Pbca*.

From the intensity calculations it is obvious that the mercury atoms occupy the positions 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$. Accordingly, space group *Fmm2* can be ruled out.

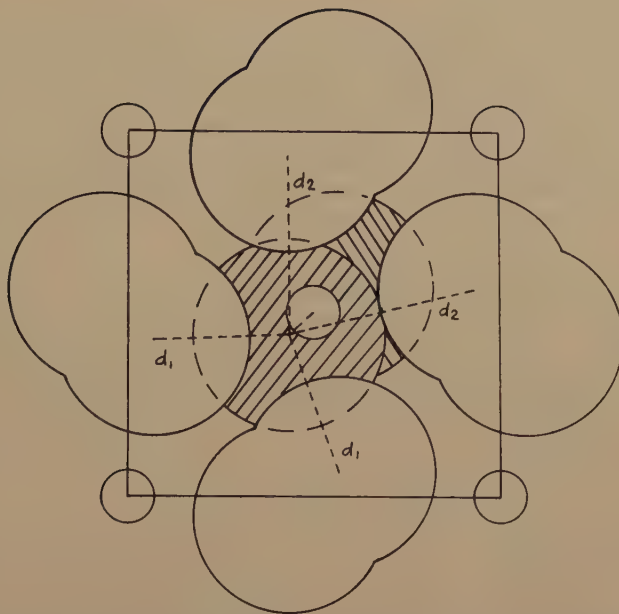


Fig. 1. Small circles indicate mercury atoms; large circles oxygen atoms. The shaded oxygen atoms are placed symmetrically around the position $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the other around the positions $\frac{1}{2}00$ and $0\frac{1}{2}0$. The van der Waals radii are drawn for the oxygen atoms, while the mercury atoms are not up to scale.

The space group *Fmmm* and *F222* requires the oxygen atoms to be placed in $\pm x00$, $\pm y00$ or $\pm z00$. The distance between the oxygen atoms in a peroxide group is 1.49 Å (8). If the oxygen atoms are placed in the positions $\pm z00$, this parameter would be 0.155. The distance mercury–oxygen is then $(0.500-0.155) \cdot 4.80 = 1.66$ Å, which is far too short. The reported distance in mercuric oxide is 2.03 Å (7). If the positions $\pm x00$ or $\pm y00$ are assumed, the distance between the oxygens in two peroxide ions would be $\sqrt{(3.04-1.49)^2 + 2.40^2} = 2.86$ Å, which cannot be accepted as a packing distance between oxygen atoms. The corresponding distance in mercuric oxide is 3.37 Å (7). The space groups *Fmmm* and *F222* may accordingly be ruled out. Then there are only the groups *Pccn* No. 56 and *Pbca* No. 61 left. Of those, the last was chosen as a trial because this space group seems to give the most probable distribution of the peroxide ions.

The oxygen parameters were now determined by "trial and error". A good fit between calculated and observed structure factors and intensities was found for $x=y=0.07$, $z=0.41$; see Table 4. Of course these oxygen parameters are rather uncertain, but they are verified by the fact that the same result can be obtained in another way, given below.

The distance between the oxygen atoms in a peroxide group is 1.49 Å (8) as mentioned above. The distance between two oxygen atoms in different groups is about 3.20 Å (9). In mercuric oxide the shortest distance between the oxygen atoms is 3.37 Å (7). In Fig. 1 the nearest neighbours of an oxygen atom can be seen. It has been assumed that the two distances d_1 are equal for symmetrical reasons and amount to 3.30 Å. This gives

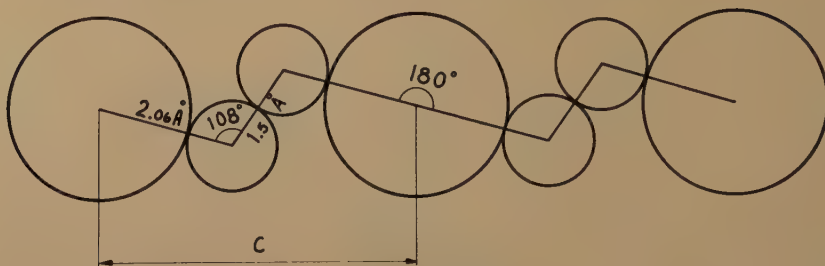


Fig. 2. Diagram showing the infinite zigzag chain -Hg-O-O-Hg- . The covalent radii are drawn for both the mercury and the oxygen atoms.

$$\begin{aligned} d_1^2 &= (\tfrac{1}{2}-2y)^2 \cdot b^2 + (\tfrac{1}{2}c)^2 \\ d_1^2 &= (\tfrac{1}{2}-2x)^2 \cdot a^2 + 4y^2 \cdot b^2 + (\tfrac{1}{2}c)^2 \\ d_1^2 &= 3.30^2 \\ 1.49^2 &= 4x^2 \cdot a^2 + 4y^2 \cdot b^2 + 4(\tfrac{1}{2}-z)^2 \cdot c^2 \\ x &= 0.075 \\ y &= 0.062 \\ z &= 0.405 \end{aligned}$$

The values are, as can be seen, in very good agreement with those found from the observed intensities.

Discussion of the structure

In the structure proposed, a mercury atom is surrounded by two oxygen atoms at a short bonding distance and four at considerably longer distances. The six oxygen atoms form a distorted octahedron. The short bonding distance is $2.06 \text{ \AA}$. The longer weak-bonding distances are 2.66 and $2.68 \text{ \AA}$. The angle between the two bonds which a mercury atom forms is 180° . The angle between the peroxide axis and the direction of the oxygen-mercury bond is 108° . The distance between the oxygen atoms in a peroxide group is $1.5 \text{ \AA}$. The oxygen atoms too are surrounded by six neighbours in some kind of octahedral symmetry. Of these neighbours, one mercury and one oxygen atom are bonded to the oxygen atom with covalent bonds. The other four are all mercury atoms at 2.66 and $2.68 \text{ \AA}$. Then there are four oxygen atoms at distances which indicate only weak van der Waals bonds. The last-mentioned distances are 3.2 , 3.4 , 3.4 and $3.5 \text{ \AA}$.

Table 5.

	$\beta\text{-HgO}_2$	HgO
Hg-coordination	2	2
Hg-O distance	$2.06 \text{ \AA}$	$2.03 \text{ \AA}$
O-O packing distance	$3.2\text{--}3.5 \text{ \AA}$	$3.39 \text{ \AA}$
Hg-O packing distance	$2.66\text{--}2.68 \text{ \AA}$	$2.82 \text{ \AA}$
$\angle \text{O-Hg-O}$	180°	179°
$\angle \text{Hg-O-O}$	108°	—
$\angle \text{Hg-O-Hg}$	—	109°

The mercury atoms and the peroxide groups form infinite zigzag chains extended along the *c*-axis (see Fig. 2). The similarity of this structure and that of mercuric oxide is striking. A comparison between the structure reported here and that of mercuric oxide as proposed by K. Aurivillius (7) is made in Table 5.

According to the structure described here, the coordination number of mercury in mercuric peroxide and the angle between the bonds indicates *sp*-hybridization for the mercury atom while the angle between the peroxide axis and the direction of the oxygen-mercury bond may indicate *sp*³ hybridization for the oxygen atoms.

SUMMARY

The α - and β -mercuric peroxides have been prepared and their crystal structures investigated. α -HgO₂ may have rhombohedral symmetry with $a = 4.74$ and α very close to 90°. β -HgO₂ has rhombic symmetry with $a = 6.080$ Å, $b = 6.010$ Å, $c = 4.800$ Å and crystallizes according to the space group *Pbca* No. 61. The mercury atoms and the peroxide groups form infinite chains extended along the *c*-axis.

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Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden, December 1958.

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Mass spectrometric studies

I. Methyl esters of saturated normal chain carboxylic acids

By RAGNAR RYHAGE and EINAR STENHAGEN

With 7 figures in the text

We have recently demonstrated the usefulness of high-mass, high-resolution mass spectrometry both for organic structure determination in the field of long chain compounds (1, 2, 3) and for the qualitative and quantitative analysis of mixtures of fatty acids (4). The methyl esters are more volatile and are less subject to thermal decomposition than the corresponding free acids, and they are therefore better suited for mass spectrometric analysis.

In the present communication we give mass spectrometric data for esters of twenty-two saturated normal chain carboxylic acids (C_5 to C_{26}). Data for the four lowest members of this homologous series are found among the mass spectral data published by the American Petroleum Institute (5).

Experimental

Material used

The methyl esters were prepared from acids having a high degree of purity. The C_{14} to C_{26} acids were those described by Stenhagen and von Sydow (6), and the lower acids were purified by distillation of the methyl or ethyl ester through a one metre electrically heated and packed column (cf. 7). The methyl esters were prepared from the free acids by means of fresh diazomethane in ether solution. After removal of excess diazomethane and ether the esters were dissolved in light petroleum (b.p. 40–60°) and the solution run through a short column of de-activated aluminium oxide in order to remove any free acid or polymethylene present. The mass spectra indicated that the amount of homologous impurity present in the methyl esters thus obtained was in most cases less than 0.5 per cent. Several of the esters contained no detectable amount of homologous impurity.

Mass spectrometry

The mass spectrometer used has been described by Ryhage (8). The amount of material needed for the analysis varied with the molecular weight of the ester, being 0.2 mg for methyl *n*-pentanoate and 1 mg for methyl *n*-hexacosanoate. Magnetic scanning was used, and the time needed for a run varied from three to seven minutes. The energy of the electrons was 70 volts, and the temperature of the intake system was kept at 200°.

Reproducibility of the mass spectra

As is well known (9), mass spectra are influenced by a number of factors, particularly the temperature of the ion source, the condition of the filament, and the focussing of the ion beam. Other variations can be due to thermal cracking, and variations due to this cause must of course be expected to occur for many organic compounds of high molecular weight. In case of extensive thermal cracking the appearance of the mass spectrum changes considerably when the spectrum is repeatedly scanned.

Table 1.

Mass spectrum	43	57	59	74	87	m/e					
						101	143	227	239	241	270
A	35	16	10	100	58	4.4	11	1.6	3.8	1.4	12
B	27	18	13	100	68	5.3	13	8.4	5.4	2.3	12
C	40	19	10	100	72	6.7	16	4.4	5.1	1.3	15
D	15	13	4.2	100	75	7.3	23	16	9.3	4.7	24
E	18	11	5.8	100	85	7.6	19	14	8.4	3.8	22

	Date of measurement	Temperature of sample inlet, °C	Galvanometer deflection in mm for m/e 74	Weight of sample mg
A	23.2. 1956	280	1,680	11
B	10.2. 1957	250	5,400	10
C	21.2. 1957	220	4,508	10
D	26.11. 1957	200	4,920	0.5
E	22.4. 1958	200	5,280	0.4

Strong water and carbon dioxide peaks at $m/e = 18$ and 44 respectively are often an indication of thermal cracking. In the case of the methyl esters now studied thermal cracking was only observed for esters with more than 21 carbon atoms and was never troublesome.

The absolute intensity of the base peak at $m/e = 74$ did not show any decrease with increasing chain length of the ester (Fig. 1a). The variation in intensity observed is probably mostly due to variation in the pressure of the gas in the intake system.

Although fairly large intensity variations may occur between corresponding peaks in spectra run with different spectrometer tubes and intake systems, or run at different temperatures, it is our experience that the characteristic pattern of the spectrum studied is not lost. In Table 1 are given data on relative intensity for several of the characteristic peaks in the spectrum of methyl palmitate run under very different conditions. The spectra A, B, and C were run using a mass spectrometer tube with an inlet system and gas leak made of metal, whereas the spectra D and E were run with the mass spectrometer tube with inlet system and gas leak of glass used in the present work.

For mass spectra run under similar conditions the variations between the spectra obtained in different runs are insignificant for the purpose of structure analysis.

Results

For the sake of completeness we reproduce in Fig. 2 the spectra of the four lowest members of the series, drawn from the mass spectral data published by the American Petroleum Institute.

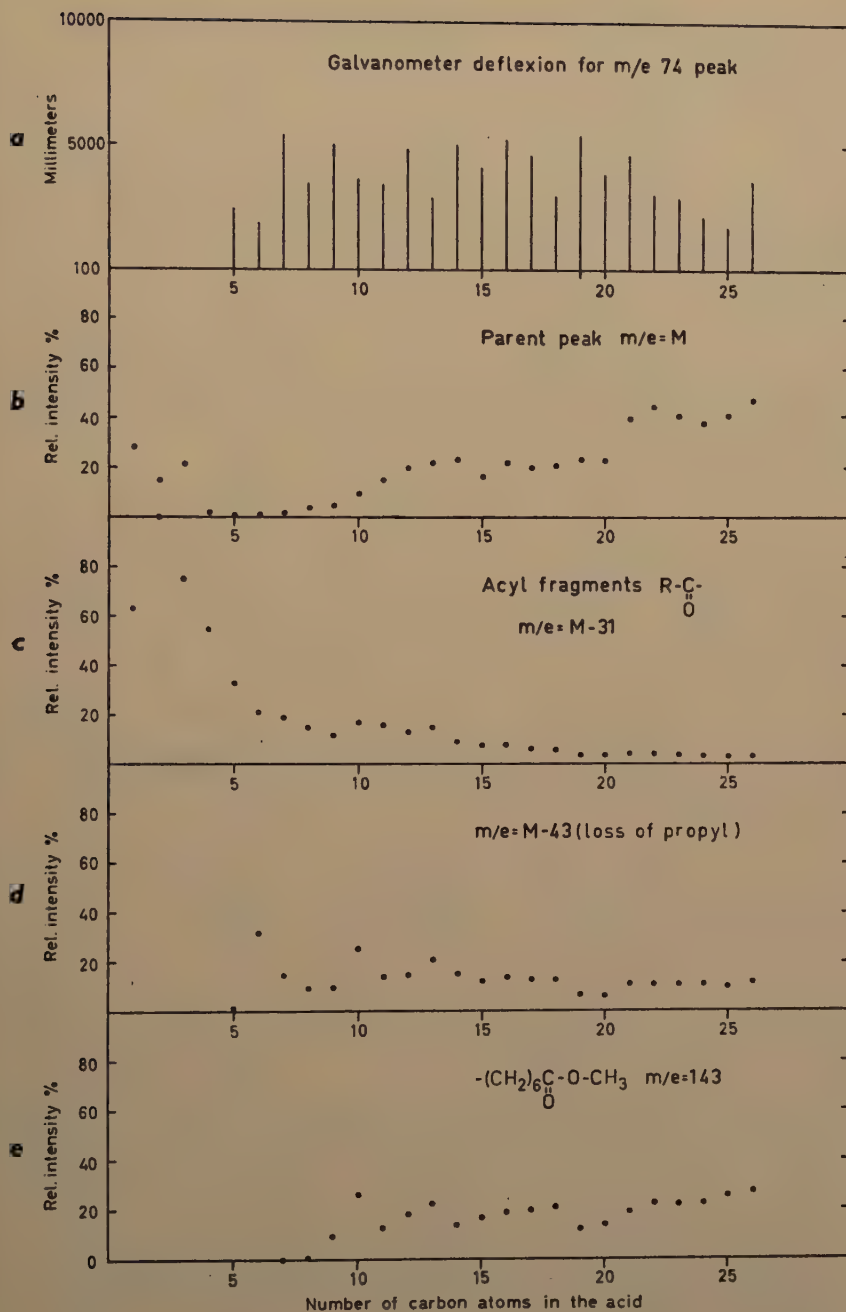


Fig. 1. Absolute intensity for the peak at $m/e = 74$, and the intensity relative to this peak of certain other characteristic peaks in the mass spectra of methyl esters of saturated normal chain acids.

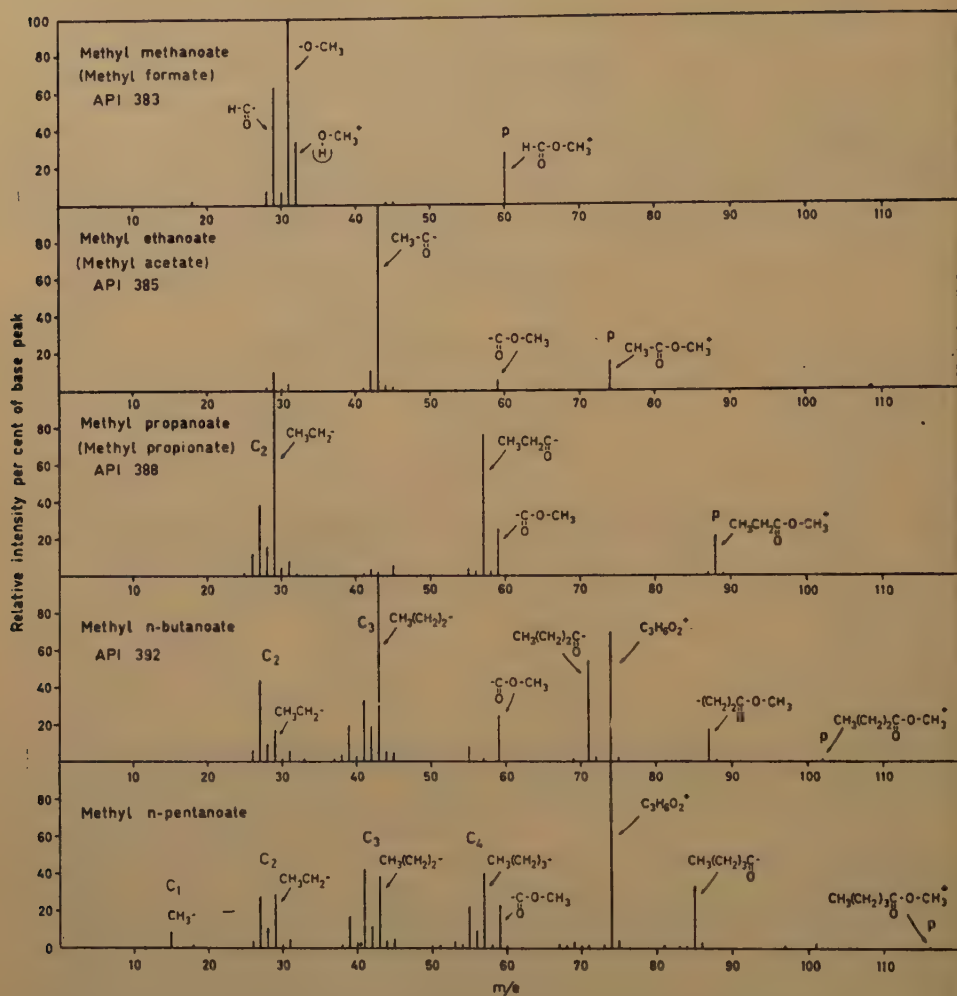


Fig. 2. Mass spectra of the five lowest methyl esters. The first four spectra have been drawn from data found in the Mass Spectral Data issued by the American Petroleum Institute.

The base peak of the spectrum of methyl formate lies at $m/e = 31$ and is evidently due to the ionized methoxyl fragment. The acylium ion $\text{H}-\text{C}^+=\text{O}$ of $m/e = 29$ is respon-

sible for the next highest peak. The strong peaks at $m/e = 32$ and $m/e = 60$ are due to a rearranged ion, HOCH_3^+ , and the molecule-ion respectively.

In the spectrum of methyl acetate the methoxyl peak is insignificant and the base peak at $m/e = 43$ is due the acetyl ion CH_3CO^+ . The peak due the molecule-ion (parent peak) is about 20 per cent of the base peak.

The peak due to the acylium ion RCO^+ is very strong in the spectrum of methyl propanoate also: but in this case the base peak is at $m/e = 29$, and appears to

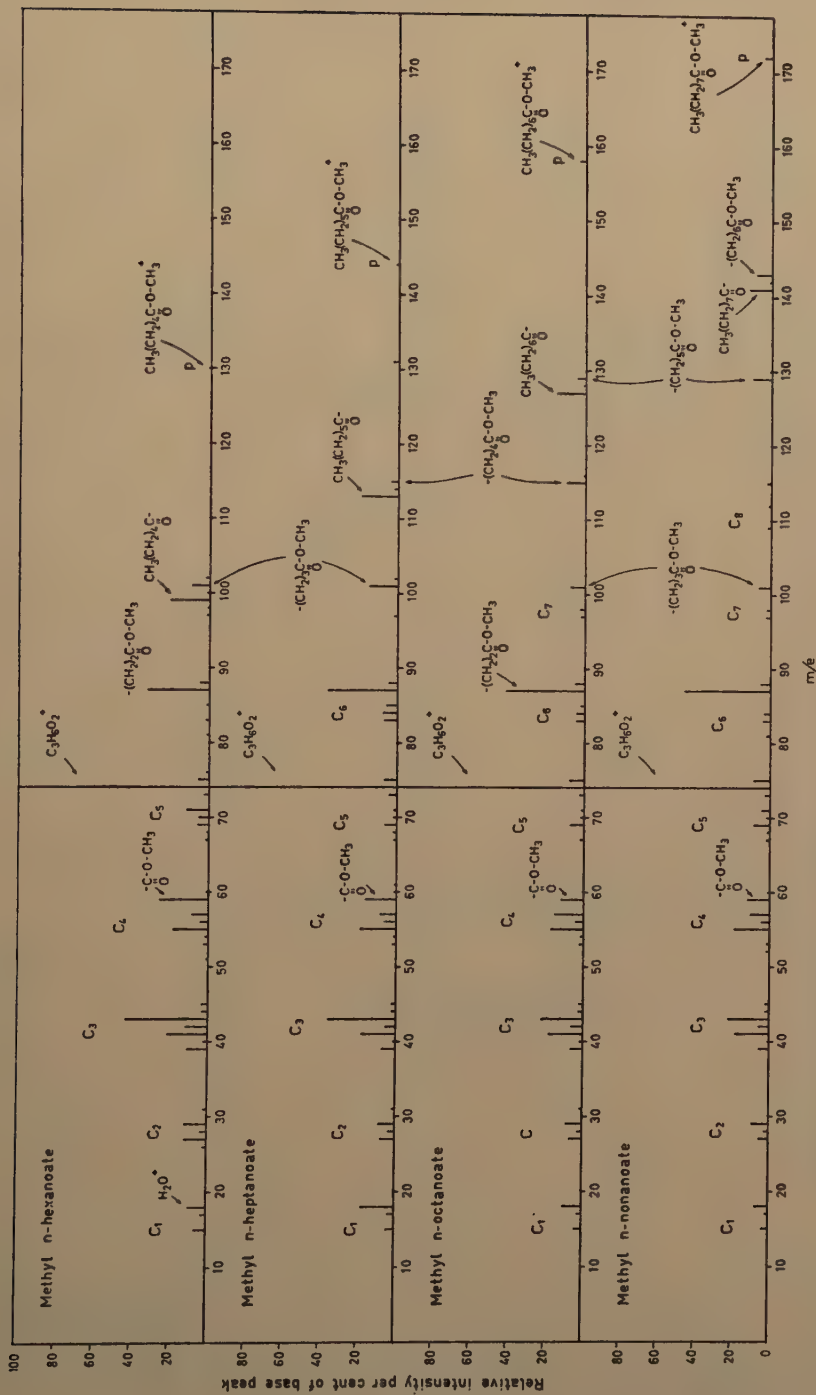


Fig. 3. Mass spectra of the methyl esters of the normal chain acids with 6, 7, 8, and 9 carbon atoms.

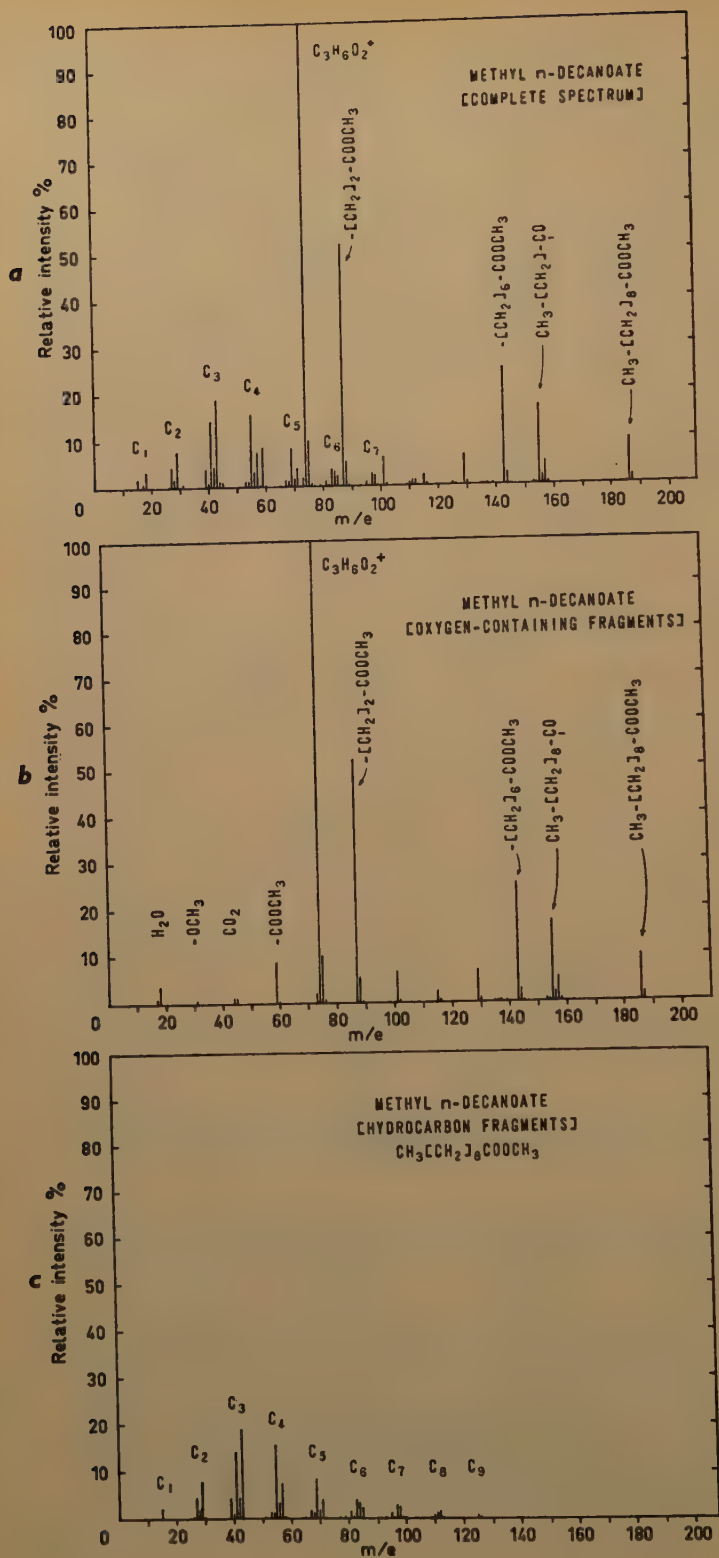


Fig. 4. Mass spectrum of methyl *n*-decanoate. a) Complete spectrum. b) Fragments containing oxygen. c) Hydrocarbon fragments.

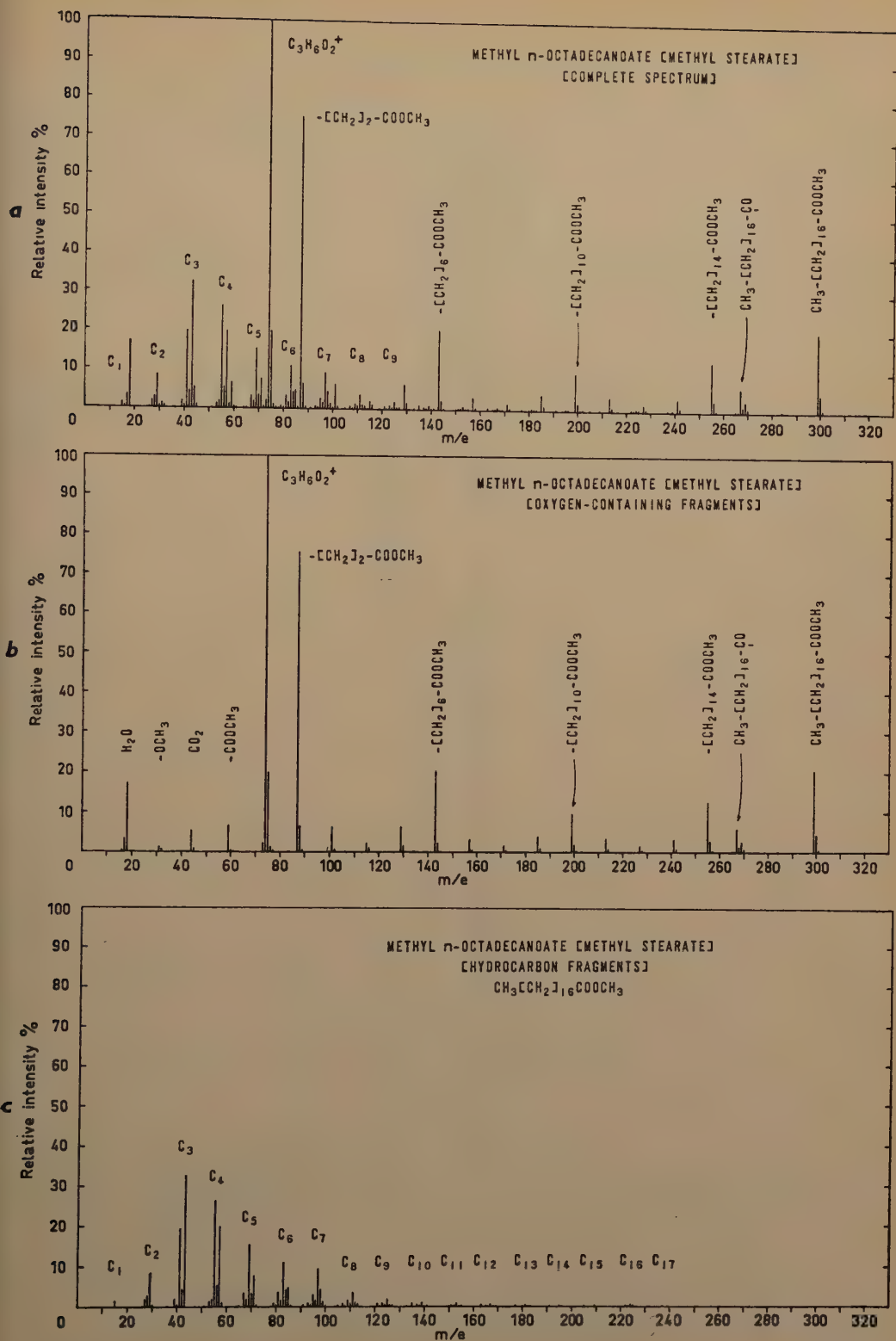
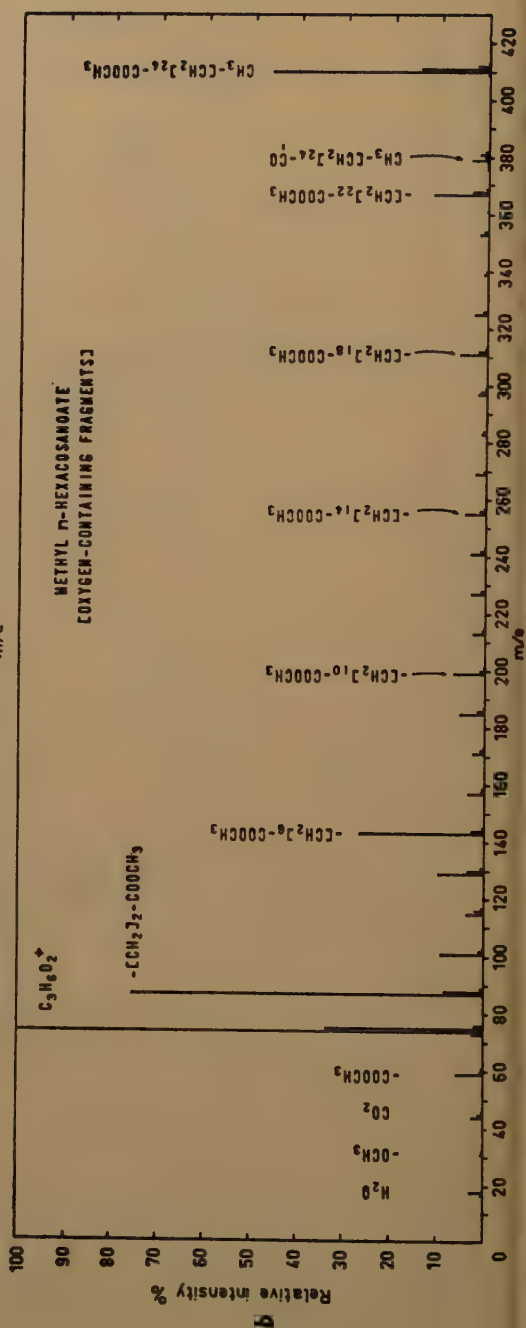
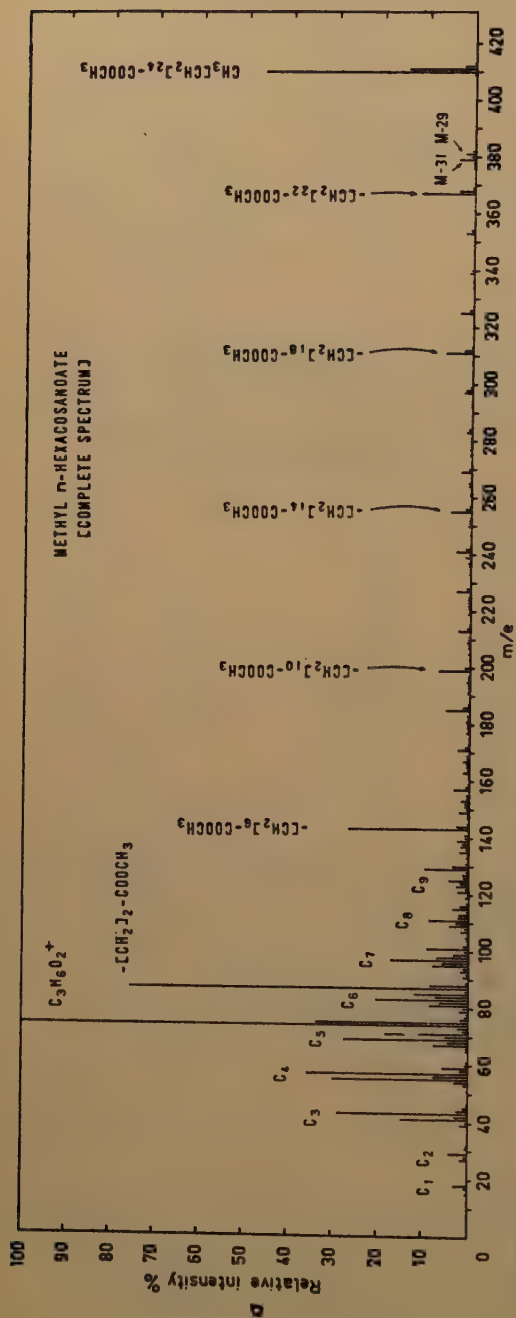


Fig. 5. Mass spectrum of methyl *n*-octadecanoate (methyl stearate). a) Complete spectrum. b) Fragments containing oxygen. c) Hydrocarbon fragments.



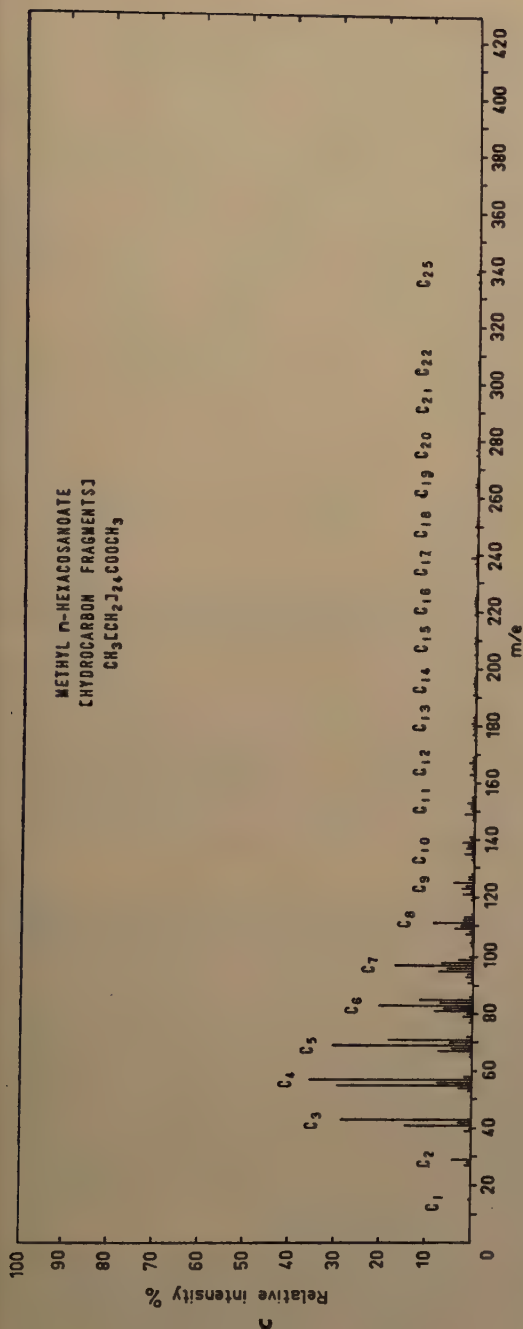


Fig. 6. Mass spectrum of methyl *n*-hexacosanoate. a) Complete spectrum. b) Fragments containing oxygen. c) Hydrocarbon fragments.

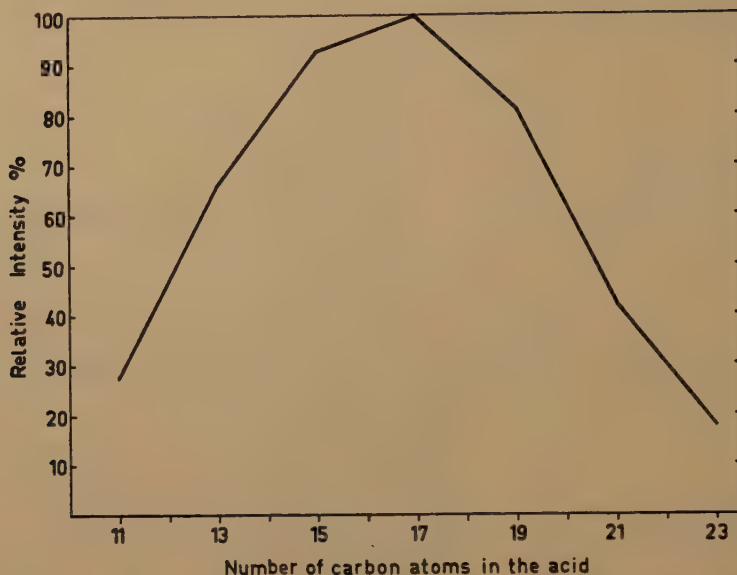


Fig. 7. Relative intensities of the parent peaks (with respect to the parent peak of methyl *n*-heptadecanoate) for the components in an equimolecular mixture of methyl esters of the normal chain odd-numbered acids with 11 and up to and including 23 carbon atoms.

arise from ethyl ions formed by 1,2-cleavage of the acyl moiety of the ester group. A corresponding state of affairs is found in the spectrum of methyl *n*-butanoate but in this spectrum is also present a strong peak at $m/e = 74$ due to a rearranged ion $C_3H_6O_2^+$. The peak due to the molecule-ion is very small. Moderately strong peaks are present at $m/e = 59$ and $m/e = 87$ which are caused by the ionized methoxycarbonyl fragment, CH_3OOC^- , and the fragment $CH_3OOCCH_2CH_2^-$ formed by loss of a methyl group respectively.

The base peak of the spectrum of methyl *n*-pentanoate and all the higher methyl esters now studied is at $m/e = 74$. This peak is analogous to the $m/e = 60$ peak of the free carboxylic acids (10). The corresponding ion is formed by 2,3-cleavage with respect to the carbonyl group and rearrangement of one hydrogen ion from the alkyl rest. The hydrogen atom is probably removed from the carbon atom 4 with the formation of a stable 1-olefin from the alkyl fragment (11). The $m/e = 74$ peak is not present in the spectrum of methyl propanoate because this molecule has a too short chain. The rearranged hydrogen atom is probably attached to one of the oxygen atoms (11).

The peak at $m/e = 87$, which is due to the normal methoxycarbonyl type fragment $CH_3OOCCH_2CH_2^-$ is as high as 30 per cent of the $m/e = 74$ peak for methyl *n*-butanoate, but its relative intensity with respect to the latter increases with chain length, and is about 75 per cent for methyl *n*-hexacosanoate.

In the mass spectra of the higher methyl esters there is a periodic variation in the intensity of the peaks due to the methoxycarbonyl fragments $CH_3OOC(CH_2)_n^-$. The peak for $n = 6$ ($m/e = 143$) is fairly strong with a height about 20 per cent of that of the base peak (Fig. 1e), and, from this peak on, every fourth methoxycarbonyl peak is higher than its neighbours. This is clearly seen in the spectra reproduced in Figs. 5b and 6b.

In the higher-mass range the highest peak is usually that due to the molecule-ion ($m/e = M$). The height of this peak goes through a minimum for methyl *n*-pentanoate and then rises with increasing molecular weight of the ester (Figs. 1 b, 3-6). For methyl *n*-hexacosanoate the parent peak is about 50 per cent of the base peak.

However, for an equimolecular mixture of the seven methyl esters of the odd-numbered acids with 11-23 carbon atoms the highest parent peak was observed for the ester of the C_{17} acid. Fig. 7 shows the intensities of the parent peaks of the other components of this mixture in per cent of that of methyl *n*-heptadecanoate. The fall-off of the intensity of the parent peaks of the higher esters in the mixture is probably due to several factors and requires further investigation.

The next highest peak in the high mass range of the higher esters lies at $m/e = M - 43$, corresponding to an ionized fragment formed with loss of a propyl group. The height of this peak is 10-15 per cent of that of the base peak, and there is no appreciable variation of the height with increase in chain length. For methyl *n*-decanoate, where $(M - 43) = 143$, the peak at $m/e = 143$ is markedly stronger than for the higher and the next lower homologue (Fig. 1, d and e).

A smaller but analogous peak at $m/e = M - 29$, due to ions formed with loss of an ethyl group, is also a constant feature of the methyl ester spectra. Like the peak at $m/e = M - 43$, the height of this peak does not vary significantly with chain length.

A peak due to the acylium ion RCO^+ is found at $m/e = M - 31$. The height of this peak decreases in regular manner with increasing chain length (Fig. 1 c).

The hydrocarbon type peaks are of appreciable intensity only at low mass numbers, the highest peak being due to propyl ($m/e = 43$) or butyl ($m/e = 57$) ions (Figs. 2, 3, 4 c, 5 c, and 6 c).

Complete intensity data for all peaks having an intensity of 0.2 per cent or more of that of the base peak are given in Table 2.

SUMMARY

Data are given of the mass spectra of a homologous series of methyl esters of saturated, normal chain carboxylic acids up to and including methyl *n*-hexacosanoate.

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Table 2 A.

n	15	14	13	12	11	10	9	8	7	6	5
M	256	242	228	214	200	186	172	158	144	130	116
m/e											
12	...	...	...	...	...	...	...	...	...	...	...
13	...	...	...	...	...	...	...	...	...	...	...
14	...	...	...	...	...	...	...	...	...	...	...
15	1.3	1.7	2.8	2.4	2.2	2.1	3.2	3.6	4.5	6.4	8.7
16	0.2	0.5	0.7	0.3	...	...	0.2	0.2	0.3	0.4	0.3
17	2.4	5.5	7.3	2.9	1.3	1.0	1.6	2.4	3.9	3.0	0.5
18	12	17	30	13	5.7	3.7	6.7	10	18	9.9	1.9
19	...	...	...	...	...	...	...	...	...	...	...
20	...	...	...	...	...	...	...	...	...	...	...
21	...	...	...	...	...	...	...	...	...	...	...
22	...	...	...	...	...	...	...	...	...	...	...
23	...	...	...	...	...	...	...	...	...	...	...
24	...	...	...	...	...	...	...	...	...	...	...
25	...	...	...	...	...	...	...	...	...	...	...
26	0.2	0.2	0.3	...	...	0.3	0.4	0.5	0.6	1.4	3.5
27	2.4	4.2	1.6	3.7	2.5	4.5	5.2	6.8	7.6	12	28
28	1.7	1.6	2.4	1.4	0.8	1.8	2.4	2.5	3.5	3.7	11
29	6.5	10	10	7.1	3.7	7.9	8.5	8.4	8.5	12	29
30	0.5	0.3	0.4	0.3	...	0.3	0.3	0.3	0.3	0.7	1.7
31	0.5	0.4	0.5	0.5	0.3	0.7	0.8	1.0	1.2	1.8	4.5
32	0.2	...	0.6	...	...	...	...	...	0.2	...	0.2
33	...	...	...	...	...	0.2	0.2	0.2	...	...	0.6
34	...	...	...	...	...	...	...	...	...	...	...
35	...	...	...	...	...	...	...	...	...	...	...
36	...	...	...	...	...	...	...	...	...	...	...
37	...	...	...	...	...	...	...	...	...	...	...
38	...	...	0.2	...	...	0.2	0.2	0.3	0.4	0.8	0.6
39	1.8	3.7	4.4	3.7	1.8	4.3	5.7	5.9	6.4	11	17
40	0.4	0.9	1.0	0.8	0.4	0.9	1.1	1.3	1.3	2.1	2.5
41	15	25	23	17	8.4	14	18	18	18	21	42
42	3.5	5.6	5.8	4.6	1.3	4.5	5.3	5.9	5.7	12	12
43	21	28	25	20	11	19	22	22	36	44	39
44	2.5	1.6	3.5	2.0	0.6	1.3	1.6	2.0	1.9	2.9	3.6
45	0.8	1.3	1.4	1.1	0.5	1.2	1.6	1.6	2.0	2.9	4.7
46	0.2	...	0.2	...	...	...	0.2	...	...	...	0.6
47	...	...	...	...	...	...	...	...	...	...	...
48	...	...	0.6	...	...	...	...	...	...	...	...
49	...	...	...	...	...	...	...	...	...	...	...
50	...	...	0.2	...	...	...	0.2	0.3	0.4	0.6	1.3
51	...	0.2	...	0.2	0.3	0.3	0.4	0.5	0.6	1.0	1.7
52	...	...	...	...	0.2	0.2	0.2	0.3	0.3	0.5	0.7
53	0.7	1.8	0.6	1.5	1.4	1.4	1.7	1.7	1.9	2.2	3.3
54	1.0	1.8	0.7	1.5	1.3	1.2	1.4	1.1	1.0	1.1	1.9
55	16	24	19	19	16	16	18	17	17	18	22
56	3.0	4.7	3.8	3.8	3.3	3.3	3.8	3.3	5.9	3.6	9.2
57	13	13	11	10	8.4	7.5	10	15	7.3	8.2	40
58	0.8	0.9	0.7	0.6	0.5	0.5	0.6	0.9	0.6	0.9	2.0
59	5.0	9.1	7.9	8.4	8.1	9.0	11	12	16	26	23
60	0.4	0.4	0.6	0.4	0.4	0.4	0.5	0.5	1.2	1.2	1.1
61	0.2	0.3	0.3	0.2	0.2	0.2	0.3	0.3	1.1	0.6	0.4
62	...	...	...	...	...	...	...	...	...	...	...
63	...	...	...	...	...	...	...	...	...	...	...
64	0.2	0.3	1.0	...	...	...	...	...	...	...	...
65	0.2	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.4	...
66	0.2	0.2	0.2	0.2	...	...	...	...	...	...	...
67	2.1	3.0	2.5	2.1	1.9	1.7	1.7	1.7	1.2	1.4	2.2
68	1.3	1.6	1.4	1.2	1.2	1.3	1.5	0.7	1.5	1.0	1.0
69	11	13	12	9.7	8.9	8.5	8.2	6.9	6.5	5.7	3.1
70	2.5	2.5	2.4	2.1	1.9	4.8	1.8	1.8	1.7	5.5	0.9
71	5.6	4.6	4.3	3.5	3.3	4.1	4.9	1.2	1.2	12	1.7
72	0.5	0.4	0.4	0.3	0.3	0.3	0.4	0.2	0.2	0.9	0.3
73	1.7	2.3	2.3	2.0	1.9	2.0	2.2	2.2	3.4	2.0	1.8
74	100	100	100	100	100	100	100	100	100	100	100
75	19	16	14	13	12	10	8.8	7.7	6.7	6.0	4.1
76	1.1	1.0	0.9	0.9	0.8	0.7	0.8	0.7	0.6	1.1	0.7
77	0.3	0.4	0.5	0.4	0.3	0.3	0.3	0.3	0.2	0.4	0.5
78	0.2	...	0.2	...	...	...	...	...	...	...	0.2
79	0.7	1.0	0.9	0.7	0.6	0.5	0.5	0.4	0.3	...	0.8
80	0.3	0.3	0.4	0.3	0.2	0.2	0.4	...	...	0.4	0.4
81	2.2	2.5	2.2	1.7	1.6	1.6	1.5	0.8	0.6	1.0	1.5
82	1.3	0.9	0.9	0.6	0.7	0.5	0.2	0.7	...	...	...
83	7.2	7.5	6.7	3.9	5.1	4.0	3.8	3.4	6.8	1.7	1.0
84	3.6	3.3	3.3	2.5	3.4	3.4	3.2	3.8	7.0	0.6	1.2
85	3.4	2.5	2.5	1.8	2.7	2.3	0.8	1.4	5.7	1.1	33
86	0.3	0.2	0.2	0.2	0.2	0.2	...	...	0.4	...	1.9
87	73	62	61	49	58	52	46	42	37	33	32
88	6.6	1.8	6.2	5.0	6.1	5.4	4.9	4.7	4.8	4.6	3.4
89	0.5	0.5	0.5	0.4	0.5	0.4	0.4	0.4	0.6	0.5	0.4

Table 2 A (continued)

n	15	14	13	12	11	10	9	8	7	6	5
m/e											
90	...	...	...	...	...	...	...	...	...	...	...
91	...	...	...	...	...	...	...	...	...	...	...
92	...	...	...	...	...	...	...	...	...	...	...
93	0.7	0.7	0.6	0.5	0.4	0.3	0.3	0.2	...	0.3	0.4
94	0.3	0.3	0.3	0.2	0.2	...	0.3	...	0.2	...	...
95	2.2	1.8	1.9	1.5	1.7	1.2	0.4	0.4	0.9	0.5	0.7
96	1.3	0.8	0.9	0.7	0.6	0.3	0.7	0.3	0.2	0.4	0.9
97	6.5	5.5	5.7	4.4	4.0	3.1	2.5	2.0	1.0	1.5	1.3
98	3.7	2.9	0.9	0.9	3.0	2.4	2.1	2.2	0.2	1.2	0.6
99	0.9	0.7	0.9	0.7	0.6	0.4	0.8	0.4	0.3	21	0.4
100	0.3	0.3	0.4	0.6	0.3	0.3	0.3	0.2	0.2	1.5	...
101	7.0	5.9	6.2	5.5	7.7	6.6	6.1	7.4	15	9.2	2.5
102	0.9	0.6	0.7	0.7	0.8	0.6	0.5	0.6	1.2	1.8	0.2
103	...	...	0.2	...	...	...	...	...	0.2	...	...
104	...	...	...	...	...	...	...	...	...	...	...
105	...	...	...	...	...	...	...	...	...	...	...
106	...	...	...	...	...	...	...	...	...	...	...
107	0.6	0.5	0.6	0.4	0.3	0.2	...	0.2	...	0.3	0.3
108	0.2	...	0.2	...	...	...	...	0.2	...	...	0.2
109	1.3	1.0	1.1	0.9	0.7	0.2	1.9	0.9	0.2	0.5	0.7
110	0.8	0.4	0.6	0.4	0.3	0.7	...	0.2	0.2	0.3	0.5
111	3.3	2.3	2.5	1.7	1.4	1.2	0.9	0.6	0.8	0.5	0.7
112	1.1	0.7	1.0	0.8	0.5	1.5	1.0	...	0.4	0.3	0.3
113	0.6	0.4	0.5	0.3	0.2	0.3	0.2	0.3	19	0.3	0.3
114	0.2	...	0.3	...	...	...	...	...	1.5	...	...
115	2.9	1.9	2.6	4.4	3.6 1	2.4	2.2	9.4	3.8	0.5	...
116	1.0	0.8	1.2	1.1	0.8	0.6	0.5	1.0	0.4	...	p 1.0
117	0.2	...	0.2	...	...	...	...	...	0.2	...	0.6
118	...	...	...	...	...	...	...	...	...	...	0.2
119	0.2	...	0.2	...	...	...	...	...	...	...	...
120	...	...	...	...	...	...	...	...	...	...	...
121	0.7	0.6	0.7	0.4	0.3	0.2	0.2	...	...	...	...
122	0.2	...	0.2	...	0.2	...	0.2	...	...	...	...
123	0.7	0.4	0.7	0.4	0.2	0.2	0.5	0.2	...	0.5	...
124	0.4	0.3	0.4	...	0.7	0.2	...	0.2	...	...	...
125	1.5	1.0	1.4	0.8	0.8	0.8	0.4	0.7	0.2	0.4	...
126	0.4	0.3	0.5	0.2	1.4	0.4	...	0.3	...	...	...
127	0.3	0.2	0.4	0.2	0.3	0.2	0.2	15	...	0.3	...
128	...	...	0.2	0.2	...	...	...	1.4	...	...	...
129	6.4	4.9	11	8.3	5.6	6.8	10	4.7	0.6	0.5	...
130	1.4	1.1	1.9	1.3	0.7	0.9	1.0	0.6	0.4	p 1.1	...
131	0.2	...	0.3	0.2	...	0.2	0.2	...	3.3	0.4	...
132	...	...	...	...	...	...	...	...	0.3	...	...
133	...	...	...	...	...	...	...	...	...	...	...
134	...	...	...	...	...	...	...	...	...	...	...
135	0.6	0.4	0.6	0.4	0.2	0.4	...	...	...	...	...
136	0.2	...	0.2	...	...	0.3	...	...	...	...	...
137	0.4	0.2	0.4	0.2	...	0.5	...	...	...	...	...
138	0.3	0.2	0.2	0.6	...	...	...	...	...	...	...
139	0.8	0.6	0.8	0.6	0.5	0.4	0.5	...	...	...	...
140	0.3	0.2	0.3	1.7	0.2	...	0.3	...	...	...	...
141	0.3	...	0.3	0.4	...	0.2	12	0.2	...	...	...
142	...	...	...	...	...	...	1.2	...	...	...	...
143	17	14	23	18	13	26	9.2	0.6	...	0.3	...
144	1.9	1.6	2.4	1.8	1.3	2.6	0.9	...	p 1.7	0.7	...
145	0.2	0.2	0.3	0.2	...	0.3	...	...	...	...	...
146	...	...	...	...	...	...	...	...	...	...	...
147	...	...	...	...	...	...	...	...	...	...	...
148	...	...	...	...	0.2	...	...	...	...	...	...
149	...	...	...	...	...	...	...	...	...	...	...
150	...	...	...	...	...	...	...	...	...	...	...
151	0.2	...	0.2	...	0.2	...	...	...	...	...	...
152	0.3	...	0.7	...	...	...	...	...	...	...	...
153	0.6	0.4	0.6	0.4	0.2	0.6	...	0.2	...	...	...
154	0.3	...	1.4	0.2	...	0.4	...	...	...	...	...
155	0.2	...	0.4	...	0.2	17	...	...	...	...	...
156	...	...	...	...	...	2.0	...	...	...	...	...
157	6.6	3.7	3.2	4.2	14	5.2	...	0.2	...	...	...
158	0.9	0.5	0.5	0.6	1.6	0.7	...	p 3.5	...	...	...
159	0.2	...	0.2	...	0.2	0.2	...	0.7	...	...	...
160	...	...	...	...	...	...	...	...	...	...	...
161	...	...	...	...	...	...	...	...	...	...	...
162	...	...	...	...	...	...	...	...	...	...	...
163	0.3	0.2	0.3	0.4	...	...	...	...	...	...	...
164	...	...	...	0.3	...	...	...	...	...	...	...
165	0.2	...	0.2	0.3	...	...	...	...	...	...	...
166	0.2	0.4	...	...	0.2	...	...	...	...	...	...
167	0.4	0.3	0.4	0.2	0.5	...	...	...	...	...	...
168	0.2	1.0	0.2	...	0.3	...	...	...	...	...	...
169	0.2	0.2	0.2	...	16	...	...	...	...	...	...

Table 2 A (continued)

n	15	14	13	12	11	10	9	n	15
m/e								m/e	
170	...	...	...	...	2.0	0.2	...	250	...
171	4.2	1.5	3.5	15	4.6	...	...	251	...
172	0.7	0.3	0.7	1.9	0.7	...	p 4.7	252	...
173	...	...	0.2	0.2	...	...	0.9	253	0.2
174	...	...	...	...	...	...	...	254	...
175	...	...	...	...	...	...	...	255	0.3
176	...	...	...	...	...	...	...	256	p 16
177	0.3	...	0.4	...	...	...	...	257	3.3
178	0.2	...	0.3	...	...	...	...	258	0.4
179	...	...	0.3	...	...	...	...		
180	0.5	...	...	...	...	...	...		
181	0.3	0.2	0.3	0.4	...	...	...		
182	0.7	...	...	0.3	...	...	...		
183	0.2	...	0.2	...	...	...	...		
184	...	...	...	13	...	...	...		
185	4.1	4.0	21	1.9	...	...	...		
186	0.7	0.7	2.9	5.8	0.3	...	...		
187	0.2	...	0.4	0.9	...	p 9.9	...		
188	...	...	...	...	...	1.8	...		
189	...	...	...	...	...	0.2	...		
190	...	...	...	...	...	...	...		
191	0.2	0.3	...	...	...	...	...		
192	...	0.2	...	...	...	...	...		
193	...	...	...	...	...	...	...		
194	0.2	...	...	...	...	...	...		
195	0.3	...	0.5	...	...	...	...		
196	0.2	...	0.3	...	...	...	...		
197	...	...	15	...	...	...	...		
198	...	...	1.9	...	0.4	...	...		
199	5.3	15	7.6	...	0.2	...	...		
200	0.7	1.8	0.7	0.8	p 15	...	...		
201	...	...	...	...	2.5	...	...		
202	...	...	...	...	0.3	...	...		
203	...	...	...	...	...	...	...		
204	...	...	...	...	...	...	...		
205	...	...	...	...	...	...	...		
206	0.3	...	...	...	...	...	...		
207	0.2	...	...	...	...	...	...		
208	0.2	...	...	...	...	...	...		
209	...	0.3	...	...	...	...	...		
210	0.2	0.2	...	...	...	...	...		
211	...	8.9	0.2	...	...	...	...		
212	0.2	1.4	...	...	...	...	...		
213	12	3.1	0.2	0.2	...	...	...		
214	1.8	0.5	0.2	p 20	...	...	...		
215	0.2	...	...	3.3	...	...	...		
216	...	...	...	0.4	...	...	...		
217	...	...	...	...	...	...	...		
218	...	...	...	...	...	...	...		
219	...	...	...	...	...	...	...		
220	...	...	...	...	...	...	...		
221	...	...	...	...	...	...	...		
222	...	...	...	...	...	...	...		
223	0.3	...	...	...	...	...	...		
224	0.2	...	...	...	...	...	...		
225	7.7	...	0.2	...	...	...	...		
226	1.3	...	...	...	...	...	...		
227	3.4	...	0.3	...	...	...	...		
228	0.6	p 22	...	...	...	...	...		
229	...	...	3.9	...	...	...	...		
230	...	...	0.5	...	...	...	...		
231	...	...	...	...	...	...	...		
232	...	...	...	...	...	...	...		
233	...	...	...	...	...	...	...		
234	...	...	...	...	...	...	...		
235	...	...	...	...	...	...	...		
236	...	...	...	...	...	...	...		
237	...	...	...	...	...	...	...		
238	...	...	...	...	...	...	...		
239	...	...	...	...	...	...	...		
240	...	...	...	...	...	...	...		
241	0.2	0.3	...	...	...	...	...		
242	0.2	p 23	...	...	...	...	...		
243	...	4.2	...	...	...	...	...		
244	...	0.5	...	...	...	...	...		
245	...	...	...	...	...	...	...		
246	...	...	...	...	...	...	...		
247	...	...	...	...	...	...	...		
248	...	...	...	...	...	...	...		
249	...	...	...	...	...	...	...		

Table 2 B.

n	26	25	24	23	22	21	20	19	18	17	16
M	410	396	382	368	354	340	326	312	298	284	270
m/e											
12	...	...	...	...	...	...	...	...	...	...	...
13	...	...	...	...	...	...	...	...	...	...	...
14	...	...	...	...	...	...	...	...	0.2	...	...
15	0.5	0.5	0.4	0.8	0.5	1.1	0.5	0.5	1.7	1.2	0.8
16	...	1.8	0.3	0.4	0.2	0.5	0.4	0.3	0.5	0.3	0.2
17	0.6	17	3.3	3.3	1.4	5.3	3.5	2.7	3.4	3.1	2.7
18	3.0	82	13	17	6.8	23	14	9.9	17	15	9.9
19	...	...	...	...	...	...	...	...	...	...	...
20	...	...	...	...	...	...	...	...	...	...	...
21	...	...	...	...	...	...	...	...	...	...	...
22	...	...	...	...	...	...	...	...	...	...	...
23	...	...	...	...	...	...	...	...	...	...	...
24	...	...	...	...	...	...	...	...	...	...	...
25	...	...	...	...	...	...	...	...	...	...	...
26	0.2	0.5	0.2	0.2	0.2	0.3	0.2	0.2	0.3	...	...
27	1.6	1.6	1.2	1.6	1.5	2.2	1.6	1.4	2.0	1.9	1.7
28	0.9	7.4	2.3	3.2	1.5	1.9	1.9	1.5	2.9	1.4	0.9
29	4.2	5.1	3.4	6.0	4.9	6.7	5.1	5.1	8.6	6.4	5.0
30	0.2	1.5	0.4	0.5	0.2	0.3	0.3	0.3	0.6	0.3	0.2
31	0.6	2.3	1.3	1.7	0.2	0.5	0.4	0.4	1.5	0.7	0.3
32	0.3	1.7	0.6	0.9	0.2	...	0.2	...	0.9	0.3	...
33	...	...	...	...	...	...	...	...	...	...	...
34	...	...	...	...	...	...	...	...	...	...	...
35	...	...	...	...	...	...	...	...	...	...	...
36	...	...	...	...	...	...	...	...	...	...	...
37	...	...	...	...	...	...	...	...	...	...	...
38	...	0.3	0.3	0.2	0.2	...	...	...	0.2	...	...
39	1.8	2.4	1.6	1.4	1.6	2.2	1.6	1.5	2.1	1.4	1.5
40	0.5	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.6	0.4	0.4
41	15	15	12	19	19	21	16	14	20	14	14
42	3.0	4.7	3.3	4.1	3.8	4.5	3.7	3.3	4.5	3.0	3.0
43	29	37	26	40	45	35	29	28	33	21	18
44	2.6	43	15	12	3.2	4.4	5.2	4.3	5.4	3.2	2.1
45	1.2	1.7	1.0	1.1	0.9	0.9	0.8	0.9	1.0	0.8	0.8
46	0.3	0.5	0.2	0.3	...	...	...	...	0.2	...	...
47	...	...	...	...	...	...	...	...	...	...	...
48	...	1.7	...	...	...	...	...	...	...	...	...
49	...	...	...	...	...	...	...	...	...	...	...
50	0.2	0.7	0.4	0.3	0.2	...	0.2	...	0.2	...	...
51	0.3	0.8	0.5	0.2	0.2	0.2	0.2	0.2	0.3	...	...
52	0.2	0.6	0.4	0.2	0.2	...	...	...	0.2	...	...
53	1.1	1.6	1.2	1.3	1.1	1.2	1.0	0.9	1.3	0.7	1.1
54	3.1	3.3	2.1	1.7	2.3	2.1	1.8	1.7	2.0	1.1	1.4
55	30	33	30	27	28	26	22	22	27	16	17
56	7.7	9.1	7.2	7.5	6.4	6.0	5.5	5.7	5.4	3.3	3.0
57	36	31	29	30	30	26	19	19	20	17	11
58	1.8	2.9	2.0	2.0	1.9	1.6	1.5	1.3	1.2	1.0	0.9
59	5.8	5.0	4.6	5.5	6.8	6.3	5.9	5.7	6.8	5.0	5.8
60	0.7	1.2	0.9	0.7	0.7	0.8	0.8	0.5	0.5	0.3	0.4
61	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3
62	...	...	...	...	...	...	...	...	...	...	...
63	...	...	...	...	...	...	...	...	...	...	...
64	...	4.3	0.8	0.2	...	0.3	0.4	...	...	...	...
65	0.6	0.8	0.5	0.3	0.3	0.3	0.3	0.5	0.3	...	...
66	0.5	0.6	0.4	0.3	0.3	0.2	0.2	0.2	0.4	0.2	0.3
67	7.8	7.2	5.7	5.0	4.9	3.9	3.8	3.3	3.6	2.9	3.3
68	4.6	4.1	3.1	2.9	2.7	2.1	2.2	1.8	2.0	1.4	1.7
69	28	27	23	21	21	19	16	15	16	14	14
70	5.0	7.9	5.8	5.1	5.0	4.1	3.4	3.5	3.5	2.8	2.9
71	19	20	18	16	14	12	9.7	9.0	8.0	7.4	6.0
72	1.3	1.5	1.2	1.1	1.1	0.8	0.8	0.7	0.6	0.5	0.5
73	2.5	2.8	2.6	2.6	2.9	2.8	2.5	2.3	2.3	1.8	2.4
74	100	100	100	100	100	100	100	100	100	100	100
75	34	35	34	35	36	28	28	23	20	22	19
76	2.0	2.2	2.0	1.6	1.7	1.4	1.4	1.3	1.3	1.1	1.0
77	0.8	1.5	1.0	0.5	0.6	0.5	0.5	0.4	0.5	0.3	0.4
78	0.5	2.0	1.2	0.5	0.4	0.3	0.4	0.2	0.3	0.2	0.2
79	2.2	2.4	2.1	1.5	1.4	1.3	1.1	1.0	1.1	0.9	1.0
80	1.3	1.2	1.1	0.7	0.7	0.4	0.5	0.4	0.5	0.4	0.4
81	8.7	8.6	6.3	5.8	4.9	4.5	3.9	3.5	3.7	2.8	2.8
82	6.4	4.4	4.1	2.0	2.2	1.6	1.8	1.5	1.7	1.4	1.0
83	21	19	18	16	15	12	12	11	11	9.0	9.7
84	7.3	6.9	5.9	5.3	5.8	4.1	4.4	4.2	4.3	3.7	4.3
85	12	13	9.4	9.0	6.6	5.9	6.0	5.4	4.9	3.9	4.4
86	0.8	1.3	1.0	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.4
87	76	74	80	71	71	63	71	74	76	74	85
88	8.5	7.2	6.6	6.8	6.4	5.7	6.2	6.9	6.6	7.0	8.0
89	0.7	0.8	0.7	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.7

Table 2 B (continued)

n	26	25	24	23	22	21	20	19	18	17	16
m/e											
90	0.2	0.2	0.2	...	...	...	...	...	...	...	...
91	...	...	...	...	...	...	...	...	...	...	...
92	0.5	0.7	0.6	0.3	0.2	...	0.2	...	...	...	...
93	2.0	1.9	1.6	1.3	1.1	1.1	1.0	0.9	1.0	0.9	1.0
94	1.2	1.2	1.1	0.6	0.6	0.4	0.5	0.4	0.5	0.3	0.4
95	8.0	7.1	5.9	3.7	4.2	3.3	3.5	2.9	3.0	2.7	3.0
96	5.8	4.2	3.6	2.4	2.2	1.5	1.8	1.5	1.7	1.3	1.4
97	17	17	14	9.8	12	9.6	9.7	8.8	9.4	6.9	8.9
98	7.1	7.0	5.9	4.7	5.4	4.2	4.5	3.7	4.5	3.6	3.8
99	3.4	3.8	2.9	2.4	2.2	1.5	1.6	1.4	1.4	1.2	1.3
100	0.9	1.4	0.9	0.6	0.7	0.4	0.4	0.4	0.4	0.3	0.4
101	9.3	9.5	8.3	8.3	7.5	6.3	6.1	6.1	6.4	7.2	7.6
102	1.2	1.4	1.2	1.1	0.9	0.7	0.8	0.7	0.7	0.8	0.9
103	0.3	0.5	0.3	0.2	0.2	0.2	0.2	...	0.2	...	0.2
104	...	...	...	...	...	...	...	...	...	...	...
105	...	...	...	...	...	...	...	...	...	...	...
106	0.4	0.7	0.4	0.2	0.2	...	...	...	...	...	...
107	2.1	1.7	1.6	1.3	1.2	1.0	0.9	0.7	0.8	0.8	0.9
108	0.9	0.6	0.5	0.4	0.4	0.3	0.3	0.2	0.3	0.2	0.3
109	4.4	4.1	3.6	2.9	2.7	1.9	1.8	1.5	1.6	1.5	1.7
110	2.9	2.4	1.9	1.4	1.3	0.9	0.9	0.7	0.8	0.7	0.8
111	8.8	8.8	7.0	6.3	5.9	4.3	4.2	3.5	3.7	3.4	3.7
112	2.4	2.5	2.1	1.7	1.7	1.2	1.3	1.0	1.2	1.1	1.2
113	2.3	2.5	1.8	1.5	1.3	0.9	0.9	0.7	0.8	0.7	0.8
114	0.5	0.7	0.5	0.3	0.4	0.3	0.3	0.6	0.3	0.2	0.2
115	3.8	3.7	3.3	3.0	3.1	2.5	2.4	2.3	2.2	2.7	3.6
116	2.0	2.1	1.7	1.6	1.6	1.3	1.3	1.1	1.2	1.3	1.4
117	0.5	0.6	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2
118	0.2	0.3	0.2	0.2	...	...	...	...	...	...	...
119	0.9	0.9	0.8	0.4	0.3	0.2	0.2	0.2	0.3	0.2	0.2
120	0.4	0.6	0.6	0.2	0.2	...	0.2	...	...	...	...
121	2.7	2.4	2.0	1.7	1.7	1.4	1.0	0.9	1.0	0.9	1.0
122	0.8	0.8	0.6	0.4	0.4	0.3	0.3	0.2	0.3	0.2	0.3
123	3.0	2.8	2.1	1.7	1.6	1.2	1.0	0.8	1.0	0.7	1.0
124	1.9	1.5	1.1	0.8	0.7	0.6	0.6	0.4	0.5	0.4	0.5
125	4.5	5.0	3.9	3.4	3.1	2.5	2.1	1.8	2.0	1.7	2.0
126	1.2	1.4	1.0	0.9	0.8	0.6	0.4	0.4	0.5	0.4	0.5
127	1.5	1.7	1.2	1.1	0.9	0.6	0.6	0.4	0.5	0.4	0.5
128	0.6	0.7	0.5	0.3	0.3	0.2	0.2	...	0.2	...	0.2
129	9.9	9.5	8.3	8.0	8.1	7.0	6.0	5.4	6.4	7.8	8.5
130	3.6	3.7	2.9	2.8	2.8	2.3	1.0	1.6	1.7	1.9	1.9
131	0.8	0.8	0.6	0.5	0.4	0.3	0.3	0.2	0.3	0.2	0.3
132	0.3	0.4	0.2	...	...	...	...	...	...	...	...
133	0.7	0.7	0.5	0.3	0.3	0.2	0.2	...	0.3	0.2	0.2
134	0.4	0.4	0.3	0.2	0.2	...	...	...	...	...	...
135	2.2	2.3	1.9	1.5	1.5	1.3	0.9	0.7	1.1	0.8	0.9
136	0.7	0.6	0.5	0.4	0.4	0.3	0.2	0.2	0.2	0.2	0.2
137	2.0	1.7	1.2	1.1	0.9	0.8	0.5	0.4	0.6	0.5	0.6
148	1.5	1.2	0.8	0.6	0.5	0.4	0.3	0.3	0.4	0.3	0.4
139	2.8	3.0	2.3	2.0	2.0	1.5	1.2	0.9	1.2	1.1	1.2
140	0.6	1.0	0.7	0.7	0.5	0.4	0.3	0.2	0.3	0.3	0.3
141	1.2	1.3	1.0	0.8	0.7	0.4	0.4	0.3	0.4	0.4	0.4
142	0.3	0.5	0.4	0.2	0.2	...	...	...	...	...	...
143	27	26	22	22	22	19	14	12	21	20	19
144	2.7	3.1	2.5	2.5	2.5	2.0	1.5	1.3	2.3	2.1	2.0
145	0.5	0.6	0.5	0.3	0.3	0.2	0.2	0.2	0.3	0.2	0.2
146	0.2	0.2	0.3	...	...	...	...	...	...	...	...
147	0.5	0.5	0.4	0.2	0.2	...	...	...	...	...	...
148	0.4	0.3	0.4	0.2	0.2	...	...	...	...	...	...
149	...	...	...	...	...	...	...	...	...	...	...
150	...	...	...	...	...	...	...	...	...	...	...
151	1.1	1.0	0.8	0.7	0.5	0.4	0.3	0.2	0.4	0.3	0.3
152	1.0	0.8	0.6	0.5	0.4	0.3	0.2	0.2	0.4	0.3	0.3
153	1.9	2.0	1.6	1.4	1.3	1.0	0.6	0.5	1.0	0.7	0.7
154	0.6	0.8	0.6	0.5	0.4	0.3	0.2	0.2	0.3	0.3	0.3
155	0.8	1.0	0.7	0.6	0.5	0.3	0.2	0.2	0.3	0.2	0.3
156	0.2	0.3	0.2	...	0.2	...	...	...	...	...	...
157	3.6	3.4	3.1	3.4	2.8	2.6	1.3	1.9	3.2	2.8	3.0
158	0.7	0.7	0.7	0.7	0.6	0.5	0.3	0.4	0.5	0.6	0.7
159	0.3	0.3	0.3	0.2	0.2	...	...	...	...	...	...
160	...	...	...	...	...	...	...	...	...	...	...
161	0.3	0.2	...	...	...	...	...	...	...	...	...
162	0.3	0.2	0.2	...	...	...	...	...	0.3	0.6	0.4
163	1.5	1.2	0.9	0.9	0.8	0.7	0.4	0.3	...	...	...
164	0.4	0.3	0.3	0.3	0.2	0.2	...	...	0.2	...	...
165	0.8	0.7	0.5	0.4	0.4	0.3	0.2	...	0.3	0.2	0.2
166	0.7	0.6	0.5	0.3	0.3	0.3	0.2	...	0.3	0.2	0.5
167	1.5	1.4	1.1	1.0	0.9	0.7	0.4	0.3	0.7	0.5	0.5
168	0.6	0.6	0.5	0.4	0.4	0.3	0.2	0.2	0.3	0.2	0.3
169	0.7	0.7	0.6	0.5	0.4	0.2	0.2	0.2	0.3	0.2	0.2

Table 2 B (continued)

n	26	25	24	23	22	21	20	19	18	17	16
m/e											
170	0.2	0.2	0.2	0.2	...	...	...	...	...	...	...
171	2.6	2.2	2.6	2.2	1.6	1.7	1.6	1.3	1.6	2.4	6.0
172	1.0	0.9	0.8	0.8	0.7	0.7	0.5	0.4	0.5	0.8	1.1
173	0.3	0.3	0.3	0.2	0.2	...	...	...	...	...	...
174	...	...	...	...	...	...	...	...	...	...	...
175	0.3	0.2	0.2	...	0.2	...	...	...	...	...	...
176	0.2	...	0.2	...	0.3	...	...	...	...	...	...
177	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.4	0.3	0.3
178	0.4	0.3	0.3	0.2	0.2	...	...	...	0.2	...	...
179	0.6	0.5	0.4	0.3	0.3	0.2	...	...	0.2	0.2	...
180	0.6	0.5	0.4	0.3	0.3	0.2	...	...	0.3	0.2	...
181	1.0	1.0	0.8	0.7	0.7	0.5	0.4	0.3	0.5	0.4	0.3
182	0.5	0.5	0.4	0.3	0.3	0.2	0.2	...	0.3	0.2	0.2
183	0.6	0.6	0.4	0.4	0.4	0.2	0.2	...	0.3	0.2	0.2
184	0.2	0.2	...	...	0.2	...	...	...	...	...	...
185	5.4	5.5	5.1	4.4	4.1	4.9	2.8	2.2	4.0	8.7	6.4
186	1.5	1.5	1.4	1.3	1.1	1.2	0.6	0.5	1.1	1.5	1.1
187	0.4	0.3	0.3	0.2	...	0.2	...	...	0.2	0.2	0.2
188	...	...	...	...	...	...	...	...	...	...	...
189	0.3	0.3	...	...	...	...	...	...	...	...	...
190	0.2	...	...	...	...	...	...	...	...	...	...
191	0.7	0.6	0.6	0.4	0.4	0.3	0.2	0.2	0.3	0.2	0.3
192	0.4	0.3	0.3	0.2	0.2	...	...	...	...	...	...
193	0.4	0.5	0.3	0.3	...	...	...	...	0.2	...	...
194	0.5	0.5	0.4	0.3	0.2	0.2	...	...	0.2	...	0.4
195	0.8	0.9	0.7	0.9	0.5	0.4	0.3	0.2	0.4	0.3	0.3
196	0.5	0.6	0.5	0.5	0.3	0.2	0.2	...	0.3	0.2	0.7
197	0.5	0.6	0.4	0.4	0.3	0.2	...	...	0.2	...	0.2
198	...	...	...	...	...	...	...	...	...	...	...
199	6.9	5.6	5.1	5.6	5.0	6.1	3.1	3.1	9.3	8.2	5.0
200	1.2	0.8	0.5	0.6	0.6	0.7	0.3	0.4	1.4	1.0	0.3
201	0.2	...	...	...	...	...	...	...	...	...	...
202	...	...	...	...	...	...	...	...	...	...	...
203	...	...	...	...	...	...	...	...	...	...	...
204	...	...	...	...	...	...	...	...	...	...	...
205	0.5	0.6	0.5	0.4	0.3	0.3	...	...	...	...	...
206	0.2	0.3	0.2	0.2	0.2	...	...	...	...	...	...
207	0.4	0.4	0.3	0.3	0.2	...	...	...	...	...	...
208	0.4	0.3	0.3	0.3	0.2	...	...	...	...	0.3	...
209	0.7	0.8	0.6	0.5	0.4	0.5	0.2	0.2	0.3	0.3	0.3
210	0.4	0.5	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.5	...
211	0.5	0.5	0.5	0.3	0.2	0.2	...	0.2	0.2	0.2	...
212	...	0.3	0.2	0.2	...	...	...	...	...	...	...
213	2.6	2.0	2.1	3.3	2.3	2.1	1.0	3.2	3.6	1.9	2.7
214	0.7	0.5	0.7	0.8	0.5	0.5	0.4	0.6	0.8	0.4	0.6
215	0.3	0.2	0.2	0.2	0.2	...	...	...	0.2	...	...
216	...	0.3	...	...	...	...	...	...	...	...	...
217	0.2	0.3	...	0.2	...	...	...	...	...	...	...
218	0.2	0.2	0.2	...	...	...	...	...	...	...	...
219	0.6	0.4	0.3	0.3	0.2	0.2	...	...	0.2	0.2	0.2
220	0.3	0.2	0.2	...	...	...	...	...	...	...	0.2
221	0.4	0.3	0.3	0.3	...	...	...	...	...	...	0.2
222	0.5	0.3	0.3	0.2	0.2	...	0.2	...	...	...	...
223	0.6	0.5	0.5	0.4	0.4	0.3	0.2	...	0.4	...	...
224	0.6	0.5	0.4	0.3	0.3	0.2	0.2	...	0.3	0.2	...
225	0.5	0.5	0.4	0.3	0.2	...	0.2	...	0.6	...	...
226	0.3	0.3	0.2	0.2	0.2	...	...	...	0.4	...	0.3
227	3.1	2.0	3.4	2.5	1.4	1.5	3.2	2.0	...	...	...
228	0.9	0.9	0.9	0.7	0.4	0.5	0.7	0.4	1.7	2.7	14
229	0.2	0.3	0.3	0.2	...	...	0.2	...	0.5	0.7	2.3
230	...	...	...	...	...	...	...	...	...	...	0.2
231	...	0.2	0.2	0.2	...	...	...	...	...	...	...
232	...	0.2	0.2	...	...	...	...	...	...	...	...
233	0.3	0.3	0.3	0.3	0.2	...	...	...	...	...	...
234	0.3	0.2	...	...	0.2	...	...	...	...	0.2	...
235	0.3	0.3	0.2	...	...	...	...	...	0.2	0.2	...
236	0.4	0.3	0.2	0.2	0.2	...	...	...	...	0.2	...
237	0.6	0.5	0.5	0.4	0.3	0.2	...	...	0.2	...	...
238	0.3	0.3	0.3	0.3	0.2	0.2	...	0.2	0.3	...	0.3
239	1.4	0.6	0.5	0.3	0.2	...	...	0.2	0.3	0.3	0.3
240	0.4	0.2	0.2	...	...	...	...	...	...	...	1.5
241	3.2	3.9	3.4	2.4	2.1	5.6	2.4	1.2	3.2	13	3.8
242	1.2	1.2	1.0	0.8	0.8	1.2	0.5	0.3	0.8	2.4	0.8
243	0.3	0.4	0.2	0.2	0.2	0.2	...	...	0.2	0.3	...
244	...	0.2	...	...	...	...	...	...	...	...	...
245	0.2	0.2	...	...	...	...	...	...	...	...	...
246	0.2	...	...	...	...	...	...	...	...	...	...
247	0.3	0.3	0.2	0.2	0.2	...	...	...	0.2	...	...
248	0.2	0.2	...	0.2	...	...	...	...	0.2	...	...
249	0.2	0.3	0.2	...	0.2	...	...	...	0.2	...	...

Table 2 B (continued)

n	26	25	24	23	22	21	20	19	18	17	16
m/e											
250	0.7	0.4	0.3	0.3	0.2	...	0.2	...	...	...	...
251	0.4	0.5	0.4	0.3	0.2	0.2	...	...	...	...	...
252	0.4	0.2	0.3	0.3	0.2	...	0.3	...	...	0.3	...
253	0.3	0.3	0.2	0.2	0.2	...	...	...	...	0.2	...
254	0.2	0.2	...	...	...	...	0.2	...	0.2	6.4	...
255	4.5	3.0	...	...	...	...	...	...	...	1.2	...
256	1.2	1.1	2.9	3.0	5.2	5.0	1.3	1.7	3	5.9	...
257	0.5	0.3	0.9	1.0	1.4	1.1	0.4	0.5	2.7	0.9	...
258	0.2	0.2	0.3	0.2	0.3	0.2	...	...	0.4	0.2	0.5
259	0.4	...	...	...	...	...	...	...	...	...	0.2
260	...	...	...	...	...	...	...	...	...	...	...
261	0.4	0.2	0.2	0.2	0.2	...	...	...	...	...	...
262	0.3	0.2	...	...	...	...	...	...	...	...	...
263	0.3	0.2	0.2	0.2	0.2	...	...	...	...	...	...
264	0.7	0.3	0.3	0.2	0.2	0.3	...	...	...	...	...
265	0.7	0.5	0.3	0.3	0.2	0.2	...	...	0.2	...	...
266	0.3	0.3	0.2	0.3	0.2	0.4	...	...	0.3	...	...
267	0.3	0.3	0.3	0.3	0.2	0.2	...	...	6.1	...	...
268	...	...	...	...	...	...	0.5	...	1.3	...	...
269	2.3	1.3	1.5	5.4	2.7	1.2	1.4	7.1	2.8	0.2	0.2
270	0.6	0.4	0.4	1.4	0.7	0.4	0.5	1.5	0.8	0.5	22
271	0.2	0.2	...	0.3	0.2	...	...	0.2	0.2	...	4.5
272	0.2	0.2	...	...	...	...	...	...	...	...	0.6
273	...	0.2	...	...	...	...	...	...	...	...	...
274	...	0.2	...	...	...	...	...	...	...	...	...
275	0.5	0.2	0.3	0.2	...	...	...	...	...	...	...
276	0.2	0.2	...	...	...	...	...	...	...	...	...
277	0.5	0.3	0.2	0.2	...	...	...	...	...	...	...
278	0.3	0.3	0.2	0.2	0.3	...	...	...	...	...	...
279	0.3	0.3	0.3	0.2	0.2	0.2	...	0.2	...	...	...
280	0.3	0.2	0.3	0.2	0.5	...	...	0.2	...	...	...
281	0.3	0.3	0.2	...	0.2	...	...	3.7	...	...	...
282	...	0.2	...	...	...	...	...	0.8	...	...	...
283	1.2	1.4	5.2	2.9	0.8	2.1	6.4	1.6	...	0.2	...
284	0.7	0.8	1.4	0.8	0.3	0.7	1.6	0.4	0.3	p 20	4.9
285	0.2	0.2	0.3	0.2	...	0.2	0.2	...	...	0.7	...
286	...	0.2	...	...	...	...	...	...	...	...	...
287	...	...	...	...	...	...	...	...	...	...	...
288	...	...	...	...	...	...	...	...	...	...	...
289	0.2	0.2	...	0.2	...	0.2	...	...	...	...	...
290	...	0.2	...	...	...	0.2	...	...	...	...	...
291	0.2	0.2	...	...	...	0.2	...	...	...	...	...
292	0.3	0.2	0.2	0.2	...	...	...	...	...	...	...
293	0.3	0.3	0.3	0.2	0.2	...	0.2	...	...	...	...
294	0.3	0.3	0.2	0.5	...	...	0.2	...	...	...	...
295	0.2	0.2	0.2	0.2	0.2	...	3.5	...	...	...	...
296	0.2	0.2	...	...	...	...	0.8	...	...	...	...
297	1.8	5.5	3.1	1.4	1.5	11	1.7	...	0.2	...	...
298	1.4	1.8	1.1	0.7	0.8	2.4	0.5	0.2	p 21	4.5	...
299	0.4	0.4	0.3	0.2	0.2	0.4	...	...	...	...	...
300	...	0.2	...	...	...	...	...	...	0.6	...	...
301	...	...	...	...	...	...	...	...	...	...	...
302	...	...	...	...	...	...	...	...	...	...	...
303	0.2	0.2	...	...	0.2	...	...	...	...	...	...
304	0.2	0.3	...	...	0.2	...	...	...	...	...	...
305	0.2	0.3	...	...	...	...	...	...	...	...	...
306	0.2	0.2	0.3	...	...	0.2	...	...	...	...	...
307	0.3	0.3	0.2	0.2	...	0.2	...	...	...	...	...
308	0.3	0.2	0.4	0.2	0.2	0.3	...	...	...	...	...
309	0.2	0.2	0.3	0.2	...	4.5	...	...	...	...	...
310	...	0.2	...	...	...	1.1	...	...	...	...	...
311	5.9	3.0	1.4	2.1	11	2.3	...	...	0.2	...	...
312	1.9	0.9	0.5	0.3	2.6	0.7	0.2	p 23	5.2	...	...
313	0.3	0.2	...	0.2	0.4	...	...	...	0.7	...	...
314	...	0.2	0.2	...	...	...	...	...	...	...	...
315	...	0.2	...	...	...	...	...	...	...	...	...
316	0.2	...	...	...	...	...	...	...	...	...	...
317	...	...	...	...	...	...	...	...	...	...	...
318	...	0.2	...	0.2	...	...	...	...	...	...	...
319	...	0.2	...	0.3	...	...	...	...	...	...	...
320	...	0.3	...	0.2	0.2	...	...	...	...	...	...
321	0.2	0.3	0.2	0.2	0.4	...	...	...	...	...	...
322	0.2	0.5	0.2	...	0.4	...	...	...	...	...	...
323	...	0.3	0.2	0.2	4.7	...	...	...	...	...	...
324	...	0.2	...	...	1.0	...	...	...	...	...	...
325	2.9	0.9	1.7	11	1.6	...	0.2	...	...	...	...
326	0.9	0.4	0.8	2.7	0.5	0.3	p 23	...	...	...	...
327	0.2	...	0.2	0.4	...	...	5.5	...	...	...	...
328	...	...	...	0.2	...	...	0.8	...	...	...	...
329	...	...	...	...	...	...	...	...	...	...	...

Table 2 B (continued)

n	26	25	24	23	22	21	n	26
m/e							m/e	
330	...	...	...	...	...	...	410	p 47
331	...	...	...	...	...	...	411	15
332	0.2	...	...	...	...	...	412	2.4
333	...	0.2	...	...	...	...	413	0.4
334	0.3	0.2	0.3	0.2	...	...		
335	0.2	0.2	...	0.4	...	...		
336	0.3	0.2	...	0.3	...	...		
337	0.2	0.2	...	4.2	...	...		
338	...	0.2	...	1.1	...	...		
339	0.9	1.7	11	2.2	...	0.3		
340	0.4	0.8	2.8	0.8	0.2	p 40		
341	...	0.2	0.5	0.2	...	10		
342	...	...	...	...	...	1.5		
343	...	...	...	...	...	0.2		
344	...	0.2	...	...	...	...		
345	...	0.2	...	...	...	...		
346	...	0.2	...	...	...	...		
347	0.2	0.3	...	...	...	...		
348	...	0.2	0.2	...	...	...		
349	0.2	0.2	0.3	...	...	...		
350	...	0.2	0.3	...	...	...		
351	...	0.2	3.3	...	...	...		
352	...	...	0.9	...	...	...		
353	1.9	10	2.1	...	0.4	...		
354	0.8	2.7	1.0	p 45	...	...		
355	0.2	0.5	0.3	10	...	...		
356	...	0.2	...	...	1.7	...		
357	...	0.2	...	...	0.3	...		
358	...	0.2	...	...	...	...		
359	0.2	0.2	...	...	...	...		
360	0.2	0.2	...	...	...	...		
361	0.3	...	...	...	...	...		
362	0.2	0.3	...	...	...	...		
363	...	0.3	...	...	...	...		
364	...	0.4	...	...	...	...		
365	...	3.3	...	...	...	...		
366	...	0.9	...	...	...	...		
367	12	1.9	...	0.3	...	...		
368	3.4	0.8	0.4	p 41	...	...		
369	0.6	0.2	...	12	...	...		
370	...	...	...	1.9	...	...		
371	...	...	...	0.4	...	...		
372	...	...	...	...	...	...		
373	...	...	...	...	...	...		
374	...	...	...	...	...	...		
375	...	...	...	...	...	...		
376	0.4	...	...	...	...	...		
377	0.4	...	...	...	...	...		
378	0.4	...	...	...	...	...		
379	3.6	...	...	...	...	...		
380	1.1	...	...	...	...	...		
381	2.2	...	0.2	...	...	...		
382	0.8	0.5	p 38	...	...	...		
383	...	...	11	...	...	...		
384	...	...	1.7	...	...	...		
385	...	...	0.3	...	...	...		
386	...	...	...	...	...	...		
387	...	...	...	...	...	...		
388	...	...	...	...	...	...		
389	...	...	...	...	...	...		
390	...	...	...	...	...	...		
391	...	...	...	...	...	...		
392	...	...	...	...	...	...		
393	...	...	...	...	...	...		
394	...	...	...	...	...	...		
395	...	0.3	...	...	...	...		
396	...	p 41	...	...	...	...		
397	...	12	...	...	...	...		
398	...	2.0	...	...	...	...		
399	...	0.3	...	...	...	...		
400	...	...	...	...	...	...		
401	...	...	...	...	...	...		
402	...	...	...	...	...	...		
403	...	...	...	...	...	...		
404	...	...	...	...	...	...		
405	...	...	...	...	...	...		
406	...	...	...	...	...	...		
407	...	...	...	...	...	...		
408	...	...	...	...	...	...		
409	0.4	...	...	...	...	...		

Synthesis of the *cis*- and *trans*-isomers of erythro-2,4,6-trimethyl- $\Delta^{2:3}$ -tetracosenoic acid

By LARS AHLQUIST,¹ CECILE ASSELINEAU,² JEAN ASSELINEAU,^{2,3}
STINA STÄLLBERG-STENHAGEN⁴ and EINAR STENHAGEN¹

With 5 figures in the text

Dextrorotatory $\alpha\beta$ -unsaturated acids are characteristic components of virulent strains of the tubercle bacillus (1, 2, 3, 9, 10). These acids have not been found in avirulent strains such as H 37 Ra (4, 5) and B.C.G. (5). The biological properties of these compounds have been studied by Sabin (6) and more recently by Hussein and Elberg (7) and by Ungar (8). It appears that acids of this type are the biologically most active components of the lipids of *M. tuberculosis*, producing the characteristic epithelioid-cell tissue reaction upon injection into animals.

The determination of the chemical structure of what was known at that time as "phthioic acid" was begun in 1935 by Spielman and Anderson (11), and has been pursued more recently particularly by Polgar *et al.* (12–15) and by Cason *et al.* (10, 16, 17). The unsaturated nature of this acid was found independently in 1950 by Cason and Sumrell (10), who therefore changed the name from phthioic acid to phthienoic acid, and by Chanley and Polgar (12) who suggested a new name, mycolipenic acid-I. The structure of the latter acid was given as 2,4,6-trimethyl- $\Delta^{2:3}$ -tetracosenoic acid by Polgar and Robinson (13, 14), who carried out the step-wise degradation from the carboxylic end. Oxidation gave a mixture of a dextrorotatory acid $C_{24}H_{48}O_2$ and a methyl ketone $C_{21}H_{43}-CO-CH_3$, establishing the terminal group $-CH(CH_3)-CH=C(CH_3)-COOH$. Bromination and dehydrobromination of the acid $C_{24}H_{48}O_2$ gave an $\alpha\beta$ -unsaturated acid, $C_{24}H_{46}O_2$, the oxidation of which yielded a mixture of a dextrorotatory acid and a methyl ketone, presumed to be $C_{21}H_{42}O_2$ and $C_{20}H_{40}O$ respectively. These results indicate that the constitution of mycolipenic acid-I is (A), with *n* probably 17. The length of the unbranched part of the chain was confirmed by Bailey, Polgar, and Robinson (18).

By means of physico-chemical studies which included ultraviolet and infrared spectrophotometry as well as measurement of the rate of saponification of the ester, Cason *et al.* (10, 16) also arrived at the conclusion that phthienoic acid is an α -methyl- $\alpha\beta$ -unsaturated acid, with two other methyl branching groups. The compari-

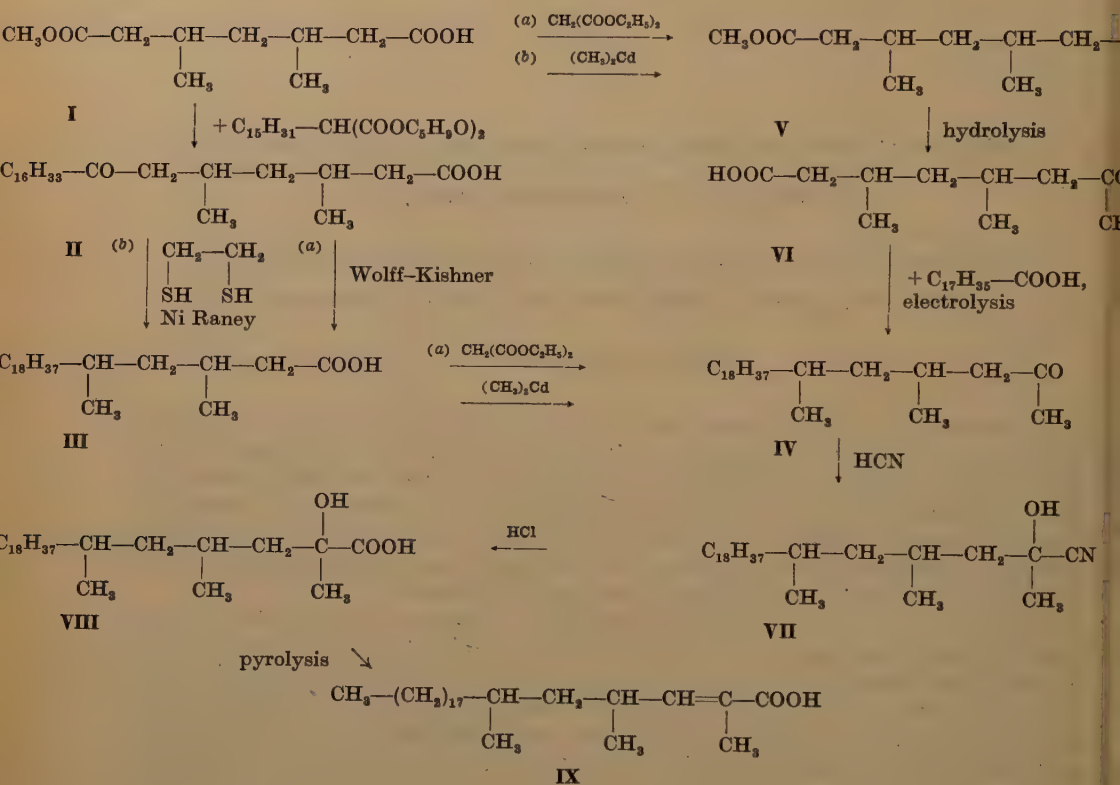
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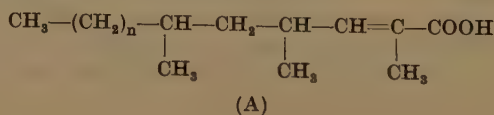
³ Rockefeller Foundation fellow, 1955–56.

⁴ Institute of Medical Biochemistry, University of Gothenburg, Sweden.

Chart I



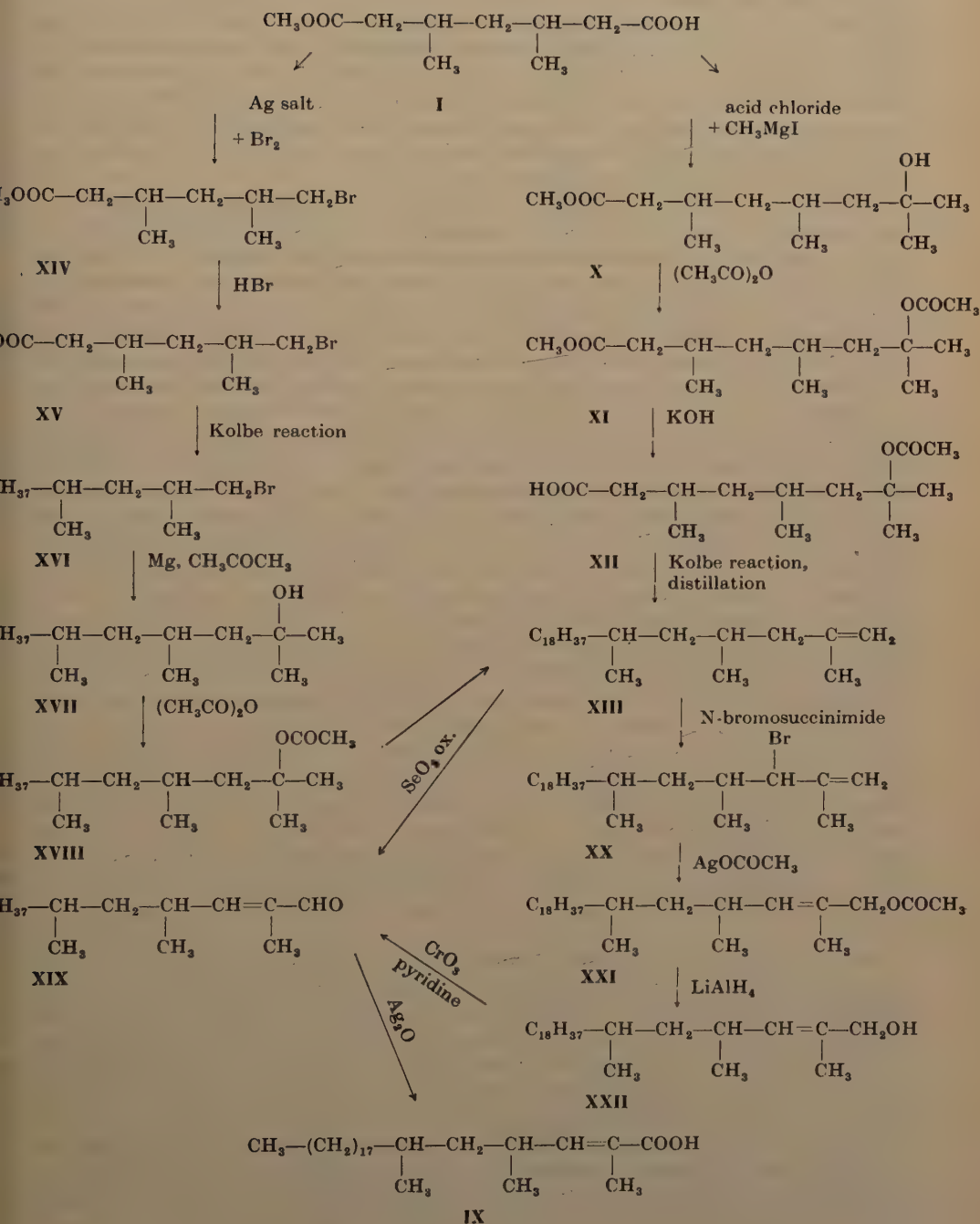
son of synthetic optically active models led Cason and Allen (17) later to place a second methyl branching group in position 4.



These results gave rise to a series of syntheses performed simultaneously by Cason *et al.* (17, 19, 20) in Berkeley, Polgar *et al.* (15, 18) in Oxford, and Ställberg-Stenhagen (22) in Uppsala. From the study of infra-red spectra of synthetic branched chain $\alpha\beta$ -unsaturated acids, it was suggested by Ställberg-Stenhagen (22) that phthienoic acid is the *trans*-isomer, a result which was confirmed by Cason and Kalm (21).

From the comparison of the optical rotation of the α -methyl branched chain acids obtained by Polgar and Robinson (13, 14) by degradation of mycolipenic acid-I, with the rotation of synthetic methyl-substituted acids (22-25), Ställberg-Stenhagen (22) deduced that the acid is likely to be *trans*-2,4,6L-trimethyl- $\Delta^{2:3}$ -tetracosenoic acid. Fray and Polgar (15) have verified this by the synthesis (14) of (+)-2L,4L-

Chart II



dimethyl-docosanoic acid, a product previously obtained in the course of the degradation of mycolipenic acid.

As a preliminary approach towards the synthesis of the optically active C_{27} - $\alpha\beta$ -unsaturated, branched chain acids, we have investigated possible routes to the synthesis of racemic *erythro*-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoic acid, starting from the methyl half-ester of *meso*-3,5-dimethylpimelic acid. All the possible stereo-isomeric methyl hydrogen 3,5-dimethylpimelates have been described (26). The synthetic routes to the C_{27} compounds are given in Charts I and II; these were briefly described in two preliminary communications (27, 28).

As indicated in Chart I, the key intermediate, 4,6-dimethyltetracosanone-2 (IV), was obtained in two different ways. Reaction of the acid chloride derived from methyl hydrogen *erythro*-3,5-dimethylpimelate (I) with the di-ester of tetrahydropyranol-2 with *n*-pentadecylmalonic acid according to Bowman and Fordham (29) gave *erythro*-3,5-dimethyl-7-oxotricosanoic acid (II), the yield being 51 %. The oxo-acid has two different crystalline forms, melting at 51.3–52.2° and 29.0–29.3° respectively. Reduction of the keto-acid performed by the Wolff-Kishner method, as modified by Huang-Minlon (30), gave *erythro*-3,5-dimethyltricosanoic acid (III), in a yield of about 70 % of the theoretical. The reduction was also carried out by the desulfurization of the ethylene-mercaptal prepared from the methyl ester of the oxo-acid, as described by Wolfrom and Karabinos (31), the yield in this case being 64 %. The reduced acid (III) is also dimorphic, the melting points being 46.4–48.4° and 27.0–27.3°. The methyl ester melts at 18.3–18.8°, and the ethyl ester at 14.8–15.3°. From the acid chloride of the acid (III), *erythro*-4,6-dimethyltetracosanone-2 (IV) has been prepared, either by malonic acid synthesis (in a yield of 60 %), or by reaction with methyl-cadmium (32) (in a yield of 68 %). The ketone melts at 20.9–21.4° and gives a semicarbazone melting at 82–83°.

A second route to the ketone (IV) involves the conversion of (I) into methyl *erythro*-3,5-dimethyl-7-oxooctanoate (V) either through reaction of the acid chloride with methyl-cadmium, or by malonic ester synthesis. Saponification of the ester (V) gave *erythro*-3,5-dimethyl-7-oxooctanoic acid (VI) in an overall yield of about 35 %. The latter was converted by mixed electrolysis with stearic acid into the ketone (IV), the yield being about 10 % of the theoretical calculated on (VI). The poor yield is probably connected with side-reactions such as cyclization. Stoll (33) has observed that Kolbe reactions involving 6-oxoheptanoic acid and, to a lesser extent, 9-oxodecanoic acid, gave low yields of the expected product. On the other hand, levulinic acid, i.e. 4-oxopentanoic acid, gives normal yields (34, 35), evidently because the keto and carboxyl groups are too near to each other to allow easy cyclization.

Reaction of the ketone (IV) with hydrocyanic acid as described by Ultée (36) gave the cyanohydrin (VII) (mixture of diastereoisomers), which was used without further purification. By heating the crude cyanohydrin with a mixture of acetic acid and hydrochloric acid, 2,4,6-trimethyl-2-hydroxytetracosanoic acid (VIII) was obtained in a yield of 35 % of the theoretical calculated on ketone (IV). The methyl ester of the hydroxy-acid melts at 22.5–23.1°. The neutral part isolated from the product of hydrolysis of the cyanohydrin mainly consisted of 2,4-dimethyltetracosanone-2.

Pyrolysis of the hydroxy-acid (VIII) was performed by heating it at about 210° for half an hour. A similar procedure was used by Lucas and Prater (37), Cason and Kalm (21) and Stållberg-Stenhagen (34) to prepare $\alpha\beta$ -unsaturated acids. The crude product was esterified by brief contact with diazomethane, and the mixture of

methyl esters was fractionated by chromatography on alumina. The separation was followed by measuring the refraction indices of the eluates, as described by Stållberg-Stenhagen (22). Methyl *erythro*-2,4,6-trimethyl-*cis*- $\Delta^{2:3}$ -tetracosenoate was the first ester eluted from the column, followed by methyl *erythro*-2-methylene-4,6-dimethyl-tetracosanoate (not isolated in a pure form), and finally, by the *trans*-isomer. The characteristics of the *cis* and *trans* esters and of the corresponding acids are given in Table 1. The pure *cis*-ester was obtained in a yield of 14 %, and the pure *trans*-ester in a yield of 5.5 % of the theoretical, calculated on the hydroxy-acid (VIII). The overall yields, calculated on the methyl half-ester (I), were 1.3 and 0.5 % respectively.

The second synthetic route is outlined in chart II, a key intermediate being in this case *erythro*-2,4,6-trimethyltetracosene-1 (XIII). This hydrocarbon was first prepared by conversion of the methyl half-ester (I) into the tertiary hydroxy-ester (X) by reaction of the acid chloride with methyl magnesium bromide. The crude hydroxy-ester (X) was acetylated by boiling with acetic anhydride, and methyl 3,5,7-trimethyl-7-acetoxyoctanoate (XI) was obtained in a yield of 51 % calculated on (I). Partial saponification under carefully standardized conditions gave the acetoxy-acid (XII) in a yield of 90 %. Mixed electrolysis of the acetoxy-acid (XII) with stearic acid in molar proportions of 1:2, followed by isolation of the reaction product by distillation and chromatography unexpectedly gave the unsaturated hydrocarbon (XIII), m.p. 10.2–10.6° in a yield of 13.5 % calculated on the acetoxy-acid (XII), together with a small amount of *erythro*-2,4,5-trimethyltetracosanol-2 (XVII) (yield 2.8 %). The alcohol (XVII) exhibits dimorphism, the two forms melting at 23.1–24.1° and 27.5–29.0° respectively. The hydrocarbon (XIII) is evidently formed by a *trans*-esterification reaction between the acetate (XVIII) and stearic acid during the distillation of the crude product. This was shown in the following manner. The acetate (XVIII), m.p. 8.6–9.2°, from the alcohol (XVII), was found to distill without decomposition at a pressure of 0.5 mm, but when mixed with stearic acid and distilled at a pressure of 10 mm, the hydrocarbon (XIII) was obtained in a yield of 75 %. The reaction is analogous to the well known pyrolysis of esters of long chain

Table 1

	<i>cis</i> -isomer	<i>trans</i> -isomer	Natural product (C ₂₇ -phthienoic acid)
<i>Methyl ester:</i>			(10)
m.p.	35.2–36.6° and 16.3–16.6°	30.5–31.5° 14.3–14.7°	30–32.5° 13–15°
$\lambda_{\max}^a$	217 m μ	215 m μ	218 m μ
	10.236	12.925	12.330
n_D^{25}	1.4587	1.4600	1.4600
<i>Free acid:</i>			(3)
m.p.	66.9–68.0°	44.5–47.2° 22.4–23.1°	39.5–42° 19–21°
$\lambda_{\max}$	221 m μ 10.720	218 m μ 13.100	218 m μ 13.200

^a All ultraviolet spectra have been measured in hexane.

alcohols with long chain acids studied by Krafft (38), which yields $\Delta^{1:2}$ -olefins. The infra-red spectrum of the hydrocarbon (XIII) shows a strong band at 11.28μ , which must be assigned to a terminal methylene group.

The alcohol (XVII) was also obtained in the following manner. Hunsdiecker degradation (39, 40) of methyl hydrogen *meso*-3,5-dimethylpimelate gave the bromo-ester (XIV) which was hydrolyzed by hydrobromic acid to erythro-3,5-dimethyl-6-bromohexanoic acid (XV), the overall yield being 31 %. The yield was later improved by a slight modification of the Hunsdiecker procedure (26). Kolbe reaction between the bromo-acid (XV) and stearic acid, used in the molar ratio 1:2, gave erythro-2,4-dimethyl-1-bromodocosane, m.p. $14.7\text{--}15.1^\circ$ (XVI), in a yield of 21 % calculated on (XV). The comparatively good yield of the Kolbe reaction does not tally with the recent work of Pattison *et al.* (41) on the behaviour of straight chain ω -halogencarboxylic acids in the Kolbe reaction, in which it was found that normal coupling occurs only if the chain possesses eleven carbon atoms or more. It thus appears that normal chain and branched ω -halogencarboxylic acids differ in this respect.

The preparation of the tertiary alcohol (XVII) from the bromo-compound (XVI) by reaction of the Grignard derivative with acetone in *n*-butyl oxide (42) gave a poor yield (6 %). The magnesium derivative was formed only with difficulty and part of the bromide was converted, possibly through a Wurtz type reaction, into a mixture of stereo-isomers of 19,21,24,26-tetramethyltetracontane (which was isolated in a yield of 17 %).

Oxidation with selenium dioxide (43) of the unsaturated hydrocarbon (XIII) gave C_{27} - $\alpha\beta$ -unsaturated aldehyde (XIX) (m.p. $29.5\text{--}35^\circ$, $\lambda_{\max}$ $225 \text{ m}\mu$ ($\epsilon = 15.550$)) in a yield of 22 %. The latter compound was further oxidized with silver oxide (44), using a slightly modified medium containing secondary butanol to increase the solubility of long chain compounds. The acidic fraction was isolated by means of chromatography on alumina, and esterified with diazomethane. Chromatography of the methyl ester gave only erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate (IX), m.p. $16.8\text{--}17.6^\circ$, $\lambda_{\max}$ $217 \text{ m}\mu$ ($\epsilon = 11.900$). The yield of this somewhat impure ester was 18 %, calculated on (XIX). The overall yield was about 0.25 %.

The C_{27} -aldehyde (XIX) was also obtained by transforming the unsaturated hydrocarbon (XIII) into the bromo-compound (XX)¹ by means of N-bromosuccinimide according to Ziegler *et al.* (46). The bromide was converted into the acetate (XXI) under conditions which favour a S_N1 reaction (47), and the acetate reduced to free alcohol (XXII) by reaction with LiAlH_4 . Racemic C_{27} -aldehyde (XIX) was then obtained by oxidation with chromic acid in pyridine according to Poos *et al.* (48). Transformation of the aldehyde (XIX) into the ester (IX) was performed as described above. Along with C_{27} -unsaturated ester, a comparatively large amount of C_{27} -saturated ester was also obtained. Formation of saturated aldehyde from allylic α -branched-chain alcohol in acidic solution might arise during the transformation of bromide (XX) into acetate (XXI) or during the oxidation of alcohol (XXII) into aldehyde (XIX) (44). This synthetic route appears to give the *trans* configuration only; the overall yield for the transformation of the unsaturated hydrocarbon (XIII) into pure racemic methyl C_{27} -mycolipenate was only 1.7 %. It must be pointed out that this route was only pursued in a very exploratory manner and it may be possible to increase the overall yield considerably. The characteristics of the sample of C_{27} -

¹ This bromide is likely to be a mixture of bromide (XX) and the primary bromide arising from allylic transposition (cf. e.g. ref. (74)).

unsaturated *trans*-ester thus obtained were: m.p. 14.1–14.6°, $\lambda_{\max}$ 216 m μ (ϵ = 12.850). The infrared spectrum is reproduced in Fig. 1e.

The infrared spectrum of the *trans*-ester in the liquid state appears identical with the spectrum of liquid methyl C₂₇-phthienoate isolated from the human strain H-37 published by Cason, Freeman, and Sumrell (16) and reproduced in our preliminary communication (27), together with that of a specimen of liquid methyl mycolipenate-I obtained by one of us (J. A.) from the human strain *Test*.

The *cis*-ester gave in the liquid state a different spectrum (Fig. 1a). This is in agreement with the previous conclusions regarding the configuration of natural C₂₇-phthienoate (21, 22). These conclusions have been strengthened by X-ray crystallographic structure determinations of the angelic and tiglic acids by Robertson and Porte (49) which clearly indicate that tiglic acid has the *trans* and angelic acid the *cis* structure.

The methyl and ethyl esters of tiglic acid have higher refraction indices than the corresponding esters of angelic acid (50, 51, 52). The ultraviolet absorption of tiglic acid is stronger than that of angelic acid (21, 22, 53).

In the course of the fractionation by adsorption chromatography of the mixture of the isomeric methyl esters, the ester having the lowest ultraviolet absorption and refraction index (*cis*) comes out first from the column, whereas the ester with the highest ultraviolet absorption and refraction index (*trans*) is the most strongly adsorbed (cf. refs. 22, 54). This behaviour is similar to the well known stronger adsorption of *trans*-isomers of compounds with a substituted double bond (cf. ref. 55).

It must be pointed out that lengthening (attachment of the long hydrocarbon chain) of the molecule of methyl hydrogen *meso*-3,5-dimethylpimelate (I) can take place, either on the same side as the free carboxyl group (Chart I, steps I→II, III→IV) or on the side of the methoxycarbonyl group (Chart I, steps I→V, VI→IV and Chart II). Both alternatives give the same final product when optically inactive ester (I) is used, but antipodes would be obtained in case the enantiomorphs of (I) were used.

After the first draft of this paper had been completed, we were notified by Professor Cason¹ of the University of California that he and his collaborators had found evidence indicating that C₂₇-phthienoic acid did not possess the structure proposed by Polgar and Robinson (13, 14). The infrared spectra are insensitive to structural features of the hydrocarbon chain beyond carbon atom 4, and the identity of the spectra of the liquid methyl C₂₇-phthienoate and our synthetic *trans*-ester in the liquid form does not, therefore, prove that the structures are identical. In order to obtain further information on this important point, we have together with R. Ryhage carried out a mass spectrometric study of several of the relevant compounds, including the synthetic methyl esters described in this communication, methyl mycolipenate isolated from the *Test* strain, one sample of methyl C₂₇-phthienoate and two samples of methyl C₂₇-phthianoate kindly provided by Professor Cason, and the methyl ester prepared from a sample of the original phthioic acid obtained in 1938 from Professor R. J. Anderson of Yale University. The mass spectrometric studies will be described in detail in a separate communication. Only the most relevant points will be dealt with here. The cracking patterns of the synthetic *cis*- and *trans*-esters (Fig. 3a and 3b) both show a strong peak at m/e 169, corresponding to a methoxycarbonyl-containing fragment arising by splitting of the chain between carbon atoms 6 and 7.

¹ Cason, J., Urscheler, H.-R., and Allen, C. F., J. Org. Chem. 22, 1284 (1957). We are indebted to Professor Cason for sending us the manuscript of this paper before publication.

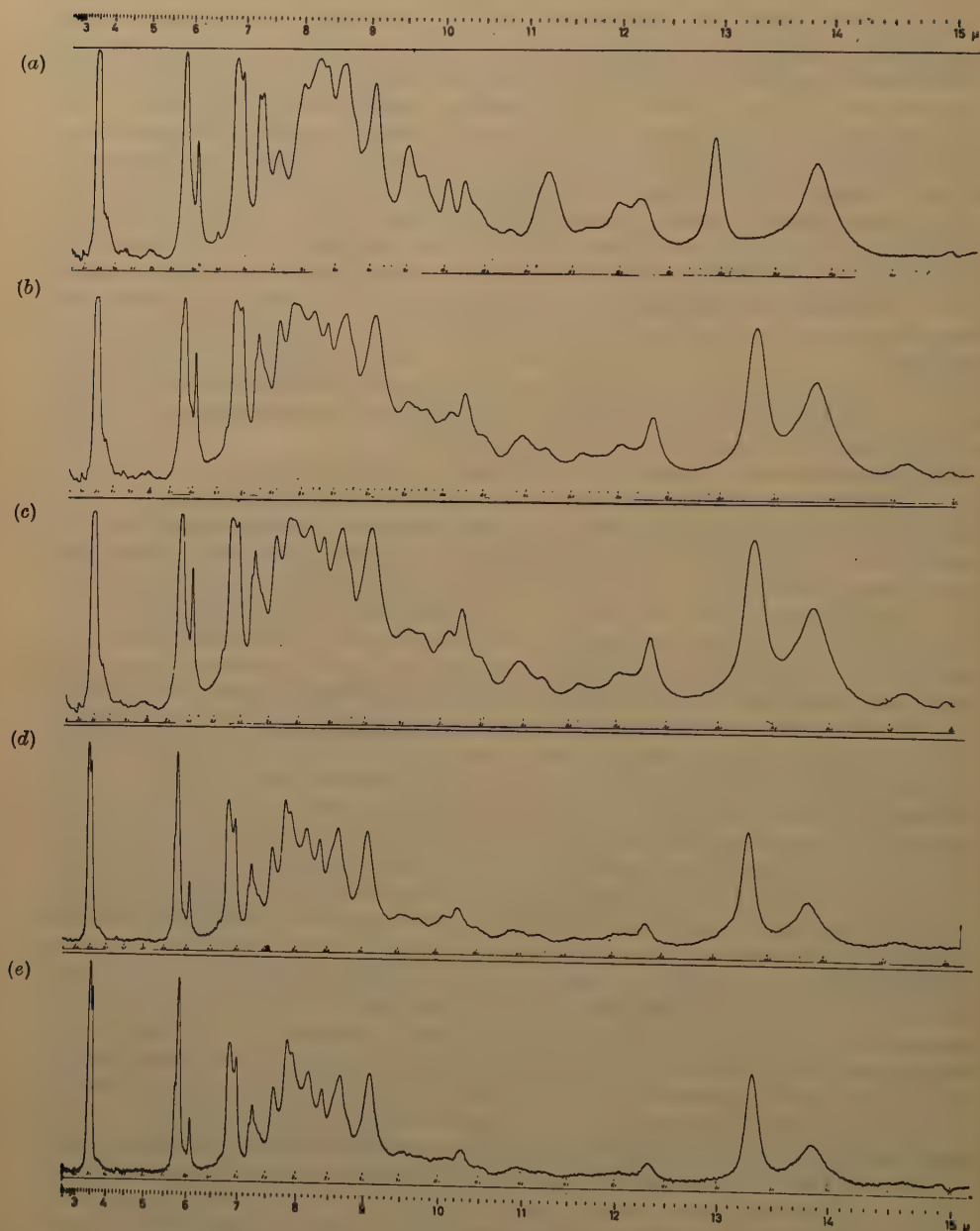


Fig. 1. Infrared spectra in the liquid state. (a) Methyl erythro-2,4,6-trimethyl-*cis*- $\Delta^{2:3}$ -tetracosenoate at a temperature of 37°. $d = 0.05$ mm. (b) Methyl erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate. (c) Methyl mycolipenate from Test strain. $d = 0.05$. (d) Methyl erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate from SeO_2 synthesis. $d = 0.02$ mm. (e) Methyl erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate from allylic transposition procedure. $d = 0.02$ mm.

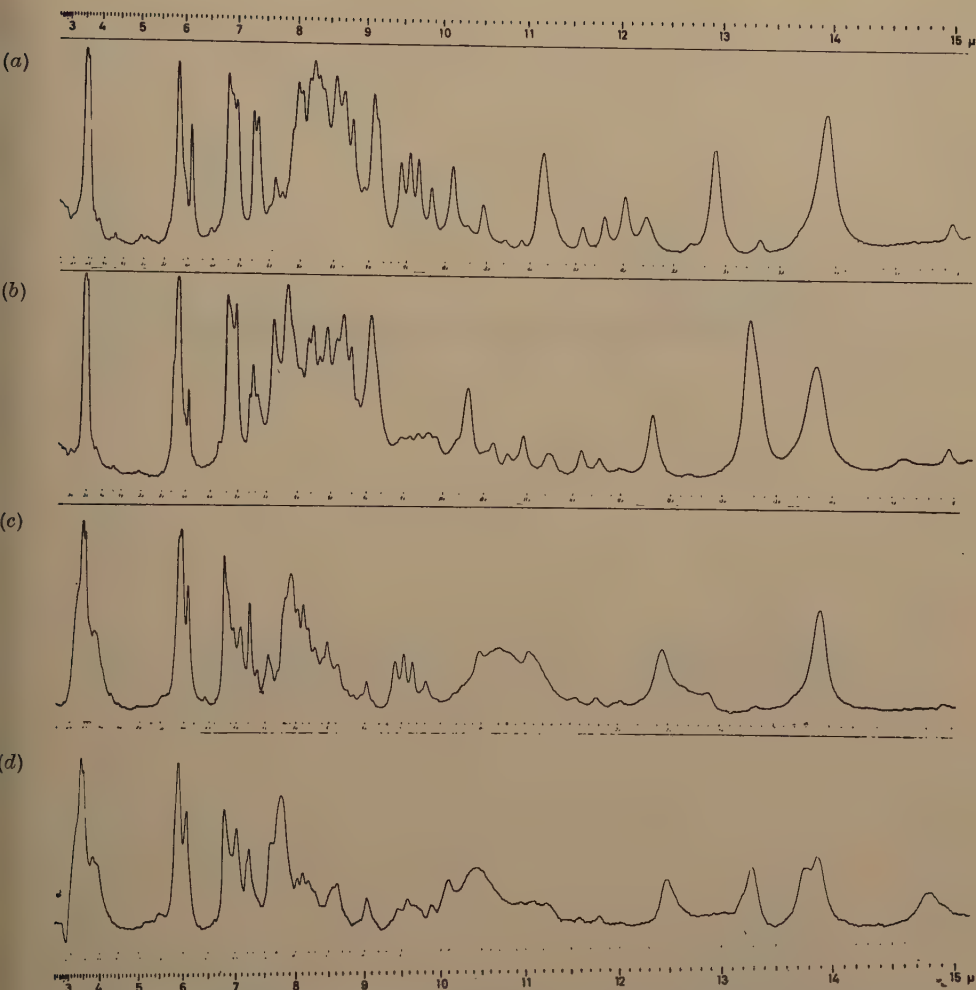


Fig. 2. Infrared spectra in the solid state. (a) Methyl *erythro*-2,4,6-trimethyl-*cis*- $\Delta^{2:3}$ -tetracosenoate 3 mg in 300 mg KBr. (b) Methyl *erythro*-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate. 3 mg in 300 mg KBr. (c) *erythro*-2,4,6-Trimethyl-*cis*- $\Delta^{2:3}$ -tetracosenoic acid. 1.6 mg in 300 mg KBr. (d) *erythro*-2,4,6-Trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoic acid. 1.6 mg in 300 mg KBr.

This peak seems characteristic of the 2,4,6-trimethyl-substituted $\alpha\beta$ -unsaturated methyl esters. It is not given by 2,4-dimethyl- or 2,5-dimethyl- $\alpha\beta$ -unsaturated esters but is present in the mass spectra of methyl C_{27} -phthienoate, methyl mycolipenate Test, and methyl phthioate. The mass spectra indicate that the Test acid is a mixture of two acids with 27 and 25 carbon atoms respectively (Fig. 3d).

Professor Cason kindly undertook the hydrogenation of part of the sample of methyl C_{27} -phthienoate whose spectrum is reproduced in Fig. 3c. The hydrogenated product gave a mass spectrum agreeing closely with that of our synthetic methyl 2,4,6-tri-

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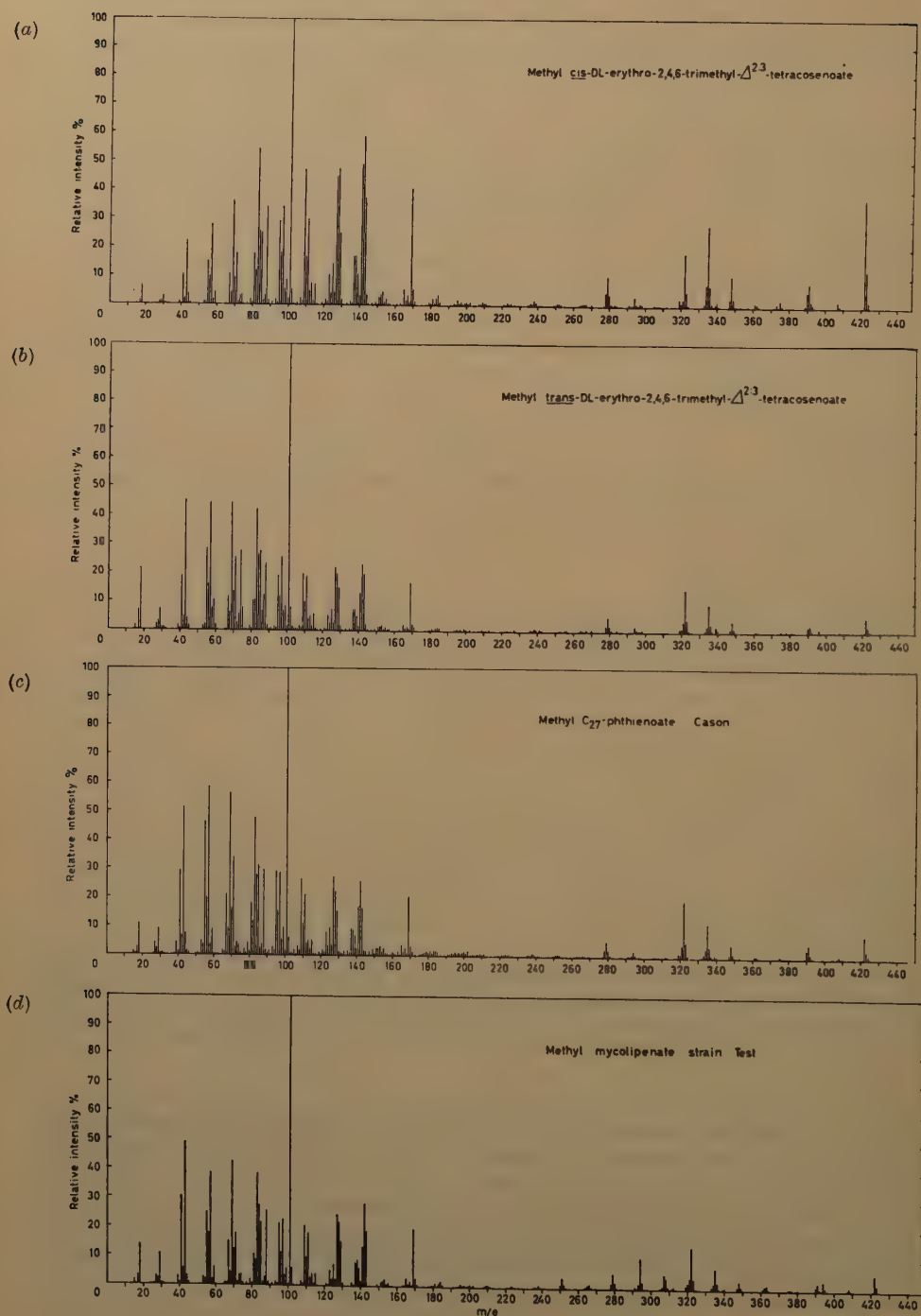


Fig. 3. Mass spectra. (a) Methyl erythro-2,4,6-trimethyl-*cis*- $\Delta^{2:3}$ -tetracosenoate. (b) Methyl erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate. (c) Methyl C₂₇-phthienoate obtained from professor Cason. (d) Methyl mycolipenate strain Test.

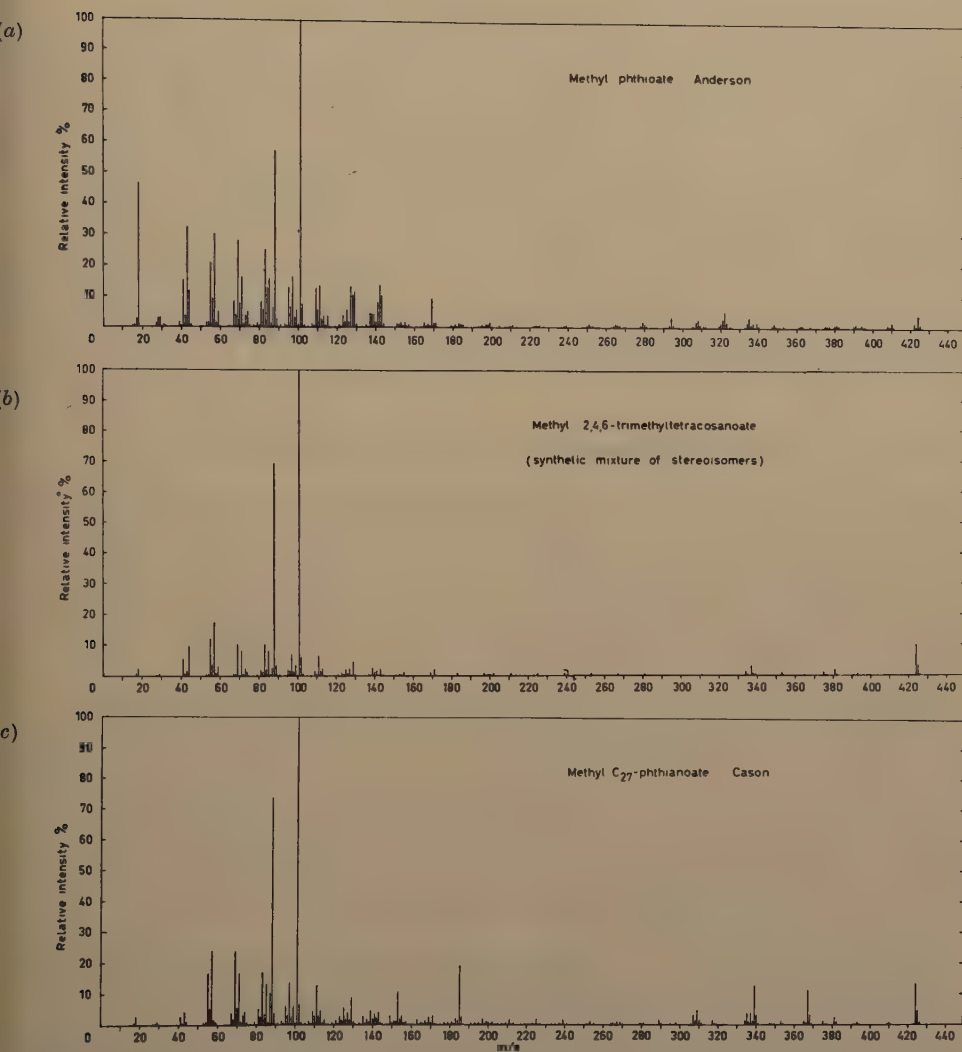


Fig. 4. Mass spectra. (a) Methyl ester of "phthioic acid" obtained from professor Anderson in 1938. (b) Methyl 2,4,6-trimethyltetracosanoate obtained by hydrogenation of *cis*-ester. (c) Methyl C₂₇-phthianoate. First sample obtained from Professor Cason.

methyltetracosanoate (Fig. 4b). On the other hand, the first sample of "methyl C₂₇-phthianoate" obtained from professor Cason gave the mass spectrum shown in Fig. 4c. It seems likely that this specimen is a mixture of methyl 2,4,6-trimethyltetracosanoate and a second component of still more complicated structure.

The mass spectra indicate that the main $\alpha\beta$ -unsaturated acid present in "phthioic acid" has the 2,4,6-trimethyl-substituted structure proposed by Polgar and Robinson for mycolipenic acid-I but that, in agreement with previous findings by Cason *et al.* (5), several other components are present.

Experimental

Melting points were determined with the aid of a liquid paraffin bath with completely immersed thermometer (23), except in the cases marked "Kofler" where a Kofler block was used. X-ray powder diffraction patterns were obtained either with a simple diffraction apparatus (23) or with a Guinier focusing camera using copper K_{α} radiation. Ultraviolet absorption measurements were carried out in hexane (spectroscopic grade) in 1 cm cells using a Beckman model DU quartz spectrophotometer (cf. ref. (22)). We are indebted to Dr. Ingrid Fischmeister and Mrs. Karin Nilsson for the infra-red spectra which were obtained with a double beam infra-red spectrometer of the type described by Horning, Hyde and Adcock (56), built by Dr. M. Skogh at Uppsala. Microanalyses recorded in this paper were carried out at the microanalytical laboratory of the Institute of Medical Chemistry at Uppsala.

erythro-3,5-Dimethyl-7-oxotricosanoic acid (II)

n-Pentadecyl bromide was prepared by the Hunsdiecker procedure (39), starting from a batch of palmitic acid of m.p. 62.4–62.8°. The acid had been carefully purified via the ethyl ester. The bromide, obtained in a yield of 75 %, had m.p. 18.2–18.7°, b.p. 143°, 0.7 mm, and n_D^{25} 1.4603 (Meyer and Reid (57) give m.p. 18.63°).

n-Pentadecylmalonic acid. The ethyl ester of *n*-pentadecylmalonic acid was prepared in a yield of 82 % by the standard procedure (58). The ester had b.p. 180–181°, 0.3 mm, and n_D^{25} 1.4420.

Saponification by heating on the water bath with aqueous potassium hydroxide for half an hour gave the free acid in a yield of about 90 %. After two crystallizations from acetone, the compound was obtained in the form of a microcrystalline powder of m.p. 112.8–113.2°. *erythro-3,5-Dimethyl-6-methoxycarbonylhexanoyl chloride* was prepared by adding 25 g of oxalyl chloride to a solution of 25 g of monomethyl ester of *meso-3,5-dimethylpimelic acid* in 30 ml of dry benzene. After 4 hours at room temperature, excess oxalyl chloride was removed in vacuo. Dry benzene was added to the residue and distilled off again. After repeating this procedure, the acid chloride was dissolved in 150 ml of benzene.

n-Pentadecylmalonic acid was transformed into the diester of tetrahydropyran-2-ol as described by Bowman and Fordham (29). 32 g of freshly distilled dihydropyran was dissolved in 120 ml of benzene, and one drop of concentrated sulphuric acid added. 39 g of *n*-pentadecylmalonic acid were then added in portions, the temperature of the mixture being kept below 30° by external cooling. The flask was swirled during the procedure. After all the *n*-pentadecylmalonic acid had dissolved, the solution was left for half an hour at room temperature. Titration of a sample of the solution then showed that only 0.628 g of free acid was present. Several grams of freshly melted, pulverized potassium hydroxide were added, and the mixture stirred during a period of 15 minutes. The solid was separated by decanting, and washed twice with 10 ml of benzene. The washings were combined to the main solution. Benzene and excess of dihydropyran were removed in vacuo on a water bath kept at a temperature of 30°.

The residue, a slightly yellow, viscous oil, was dissolved in 120 ml of benzene and the solution added to a stirred suspension of 2.9 g of powdered sodium in 240 ml of benzene. After mechanical stirring for 2 hours at room temperature, almost all

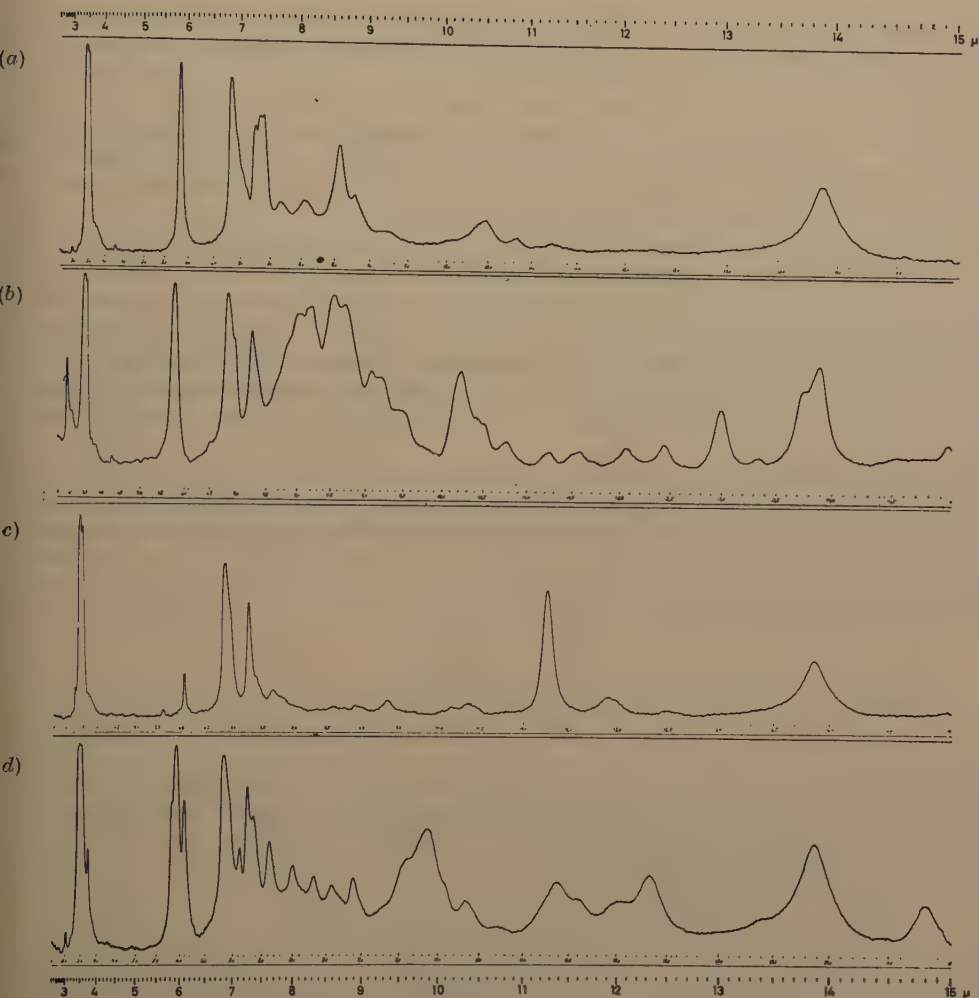


Fig. 5. Infrared spectra. (a) *erythro*-4,6-Dimethyltetracosanone-2 in the liquid state. $d = 0.02$ mm. (b) Methyl *erythro*-2,4,6-trimethyl-2-hydroxytetracosanoate. 3.6 mg in 300 mg KBr. (c) *erythro*-2,4,6-Trimethyltetracosene-1. $d = 0.02$ mm. (d) *erythro*-2,4,6-Trimethyl- $\Delta^{2:3}$ -tetracosenal-1 in the liquid state at a temperature of 31° . $d = 0.02$ mm.

the sodium had disappeared. The benzene solution of the acid chloride, described above, was slowly introduced by a dropping funnel. The content became a gel without any visible precipitation of sodium chloride. After standing overnight, 15 ml of acetic acid was added, and the mixture refluxed for $1\frac{1}{2}$ hour. A vigorous evolution of carbon dioxide was observed initially.

After cooling to room temperature, the mixture was separated into acidic and neutral parts by washing twice with 50 ml of an aqueous solution of sodium hydroxide (5 %, w/v):

1) *Acidic fraction* "A" was obtained after acidification and extraction of the alkaline extracts with ether. This fraction gave 18 g of a white amorphous product, melting at 65–70°, which was not examined further.

2) The benzene phase, after washing with water, drying over Na_2SO_4 and evaporation in vacuo, gave 48 g of a neutral fraction, obtained as an oil. After addition of a large amount of light petroleum (b.p. 40–60°), a small amount of the product crystallized, and was collected by filtration (unsaponifiable product m.p. 85°, about 50 mg).

The filtrate was evaporated in vacuo, and the residue saponified by heating on the water bath with a solution of 13 g of sodium hydroxide in 30 ml of water and 20 ml of ethanol for 1 hour. After cooling and addition of water, the mixture was separated by extraction with ether into *acidic fraction* "B" and a *neutral fraction*.

The neutral fraction weighed 1.7 g. It was obtained as an oil that rapidly crystallized. After several crystallizations from acetone and from a mixture of ethyl acetate and ethanol beautiful fine needles were obtained which melted at 73–74° (Kofler) (unsaponifiable product m.p. 74°).

After 3 crystallizations of acidic fraction "B" (40 g) from methanol (after addition of several drops of water and cooling in the refrigerator), 25 g (51 % of the theoretical, calculated on the monomethyl ester (I) of *meso*-3,5-dimethylpimelic acid) of pure *erythro*-3,5-dimethyl-7-oxotricosanoic acid (II) was obtained in the form of very small needles melting at 51.3–52.2°. An unstable form (m.p. 29.0–29.3°) was obtained on rapid solidification of the melt.

<i>Anal.</i> : Calcd. for $\text{C}_{25}\text{H}_{48}\text{O}_3$ (396.6)	C, 75.70;	H, 12.20 %
Found	C, 75.54;	H, 12.15 %
	75.70	12.22

The *semicarbazone* of the oxo-acid was prepared by means of an alcoholic solution of semicarbazide. After 2 crystallizations from ethanol, it was obtained in the form of clusters of broad needles melting at 104–109° (Kofler). The melting point could not be improved by further crystallization.

<i>Anal.</i> : Calcd. for $\text{C}_{27}\text{H}_{55}\text{O}_3\text{N}_3$ (468.7)	C, 69.33;	H, 11.42;	N, 8.98 %
Found	C, 69.34;	H, 11.03;	N, 9.2
	69.44	11.09	9.0

The same *semicarbazone* was obtained in good yield from a sample of the mother liquors from the crystallization of the oxo-acid (II). If the amount of keto-acid remaining in the mother liquor is taken into account, the yield in the Bowman-Fordham coupling becomes about 65 % of the theoretical.

Unsaponifiable product m.p. 85°

After several crystallizations from acetone this product was obtained in the form of very small leaves, which melted at 85–86° (Kofler). The compound was insoluble in light petroleum (b.p. 40–60°) and ether.

<i>Anal.</i> :	
Found	C, 82.85; H, 13.24
	82.5 13.2

The ultraviolet spectrum showed no absorption maximum between 215 and 320 $m\mu$. The infrared spectrum exhibited a strong band at 6.08 μ which might be assigned to an oxo-group.

Unaponifiable product m.p. 74°.

<i>Anal.</i> : Calcd. for $C_{24}H_{48}O$	C, 81.74;	H, 13.72;	(C)CH ₃ , 4.26 %;	M.W. 352.6
Found	C, 81.30;	H, 13.40;	(C)CH ₃ , 7.44;	M.W. (Rast)
	81.5	13.4	7.35	340
	81.6	13.3	7.21	

The ultraviolet spectrum showed no absorption maximum between 205 and 300 $m\mu$.

The infra-red spectrum exhibited bands at 2.92 and 5.96 μ . No semicarbazone could be prepared (under the conditions used for the preparation of the semicarbazone of 3,5-dimethyl-7-oxotricosanoic acid), and no oxygen uptake was observed by treatment with perphthalic acid.

Reduction of the unaponifiable product (m.p. 74°) by means of $LiAlH_4$ in ether, at room temperature, gave, as main product, a compound which after crystallization from acetone was obtained in the form of small leaves melting at 63–66° (Kofler).

<i>Anal.</i> : Calcd. for $C_{24}H_{50}O$ (354.6)	C, 81.28;	H, 14.21 %
Found	C, 81.2;	H, 13.6
	81.3	13.7

The "unaponifiable product, m.p. 74°" was recovered unchanged after reflux with acetic anhydride for 2½ hours.

erythro-3,5-Dimethyltricosanoic acid (III)

(a) Reduction according to Wolff-Kishner

To a solution of potassium hydroxide (3 g) in freshly distilled diethylene glycol (25 ml) were added 3 ml of 85 % hydrazine hydrate and 4.1 g of keto-acid (II). The mixture was heated under reflux (temperature of the metal bath 140–145°) for 2 hours. The condenser was disconnected, and heating continued until the internal temperature rose to 215°. The condenser was put on again and the mixture heated under reflux for 3 hours more.

The organic product was isolated in the form of a pale yellow oil. To the crude product thus obtained was added a solution of hydroxylamine hydrochloride (3 g) and sodium acetate (crystallized, 4.5 g) in 70 ml of 80 % ethanol (v/v). The mixture was refluxed for 2 hours. The organic product was isolated and treated with an excess of a solution of diazomethane in ether. The crude esters were chromatographed on 120 g of alumina (Merck), see Table 2.

Fraction 1 gave pure methyl *erythro-3,5-dimethyltricosanoate*, in the form of a colourless oil, n_D^{25} 1.4507.

<i>Anal.</i> : Calcd. for $C_{26}H_{52}O_2$ (396.7)	C, 78.72;	H, 13.21 %
Found	C, 79.05;	H, 13.32

Table 2

Fraction no.	Volume of eluent (ml)	Solvent	Weight of the eluated product (mg)	n_D^{25}
1	200	Light petroleum (b.p. 30–50°)	1931 colour less oil	1.4508
2	200	Light petroleum	711 " " "	1.4489
3	200	Light petroleum	169 " " "	1.4485
4	200	Light petroleum	47 " " "	1.4485
5	300	Light petroleum–benzene 1:1	16 " " "	
6	300	Benzene	43 " " "	
7	200	Benzene–ether 19:1	55 pale	
8	200	1:1	410 oil	
9	300	Ether	790 yellow oil	
Total			4172	

Fractions 7 + 8 distilled at 225–235° (temperature of the air bath), 0.5 mm. The distillate was an almost colourless oil, n_D^{25} 1.4625.

<i>Anal.</i> : Calcd. for $C_{26}H_{52}O_3$ (412.7)	C, 75.67; H, 12.70
Found	C, 75.4; H, 12.2
	75.4 12.2

The elementary composition of this fraction, and its behaviour on alumina columns, show that it consists of a mixture of stereoisomers of methyl 3,5-dimethyl-7-hydroxy-tricosanoate.

Methyl *erythro*-3,5-dimethyltricosanoate was subjected to alkaline hydrolysis. A small amount of an unsaponifiable product was separated by extraction of the alkaline hydrolysis mixture with ether. Acidification and three crystallizations of the free acid from acetone (with addition of several drops of water and cooling to about +4°) gave a white crystalline powder, melting at 46.4–48.4°. After rapid cooling of the melt, the solidified product melted at 27.0–27.3°. The dimorphism of the acid was checked with the aid of X-ray powder diffraction photographs.

(b) Reduction by the Wolfrom-Karabinos method

erythro-3,5-Dimethyl-7-oxotricosanoic acid (6.3 g) was esterified by means of diazomethane. The crude keto-ester was dissolved in 5 ml of dry ether and 5 ml of ethanedithiol. A slow current of gaseous hydrogen chloride was passed through the solution during two hours (59, 60). The flask was put in an exsiccator over sodium hydroxide *in vacuo* for 48 hours. Excess of ethanedithiol was removed by heating at about 30°, 0.1 mm. Xylene was added, and distilled off. This procedure was repeated twice.

30 g of Raney nickel was prepared from 60 g of a 50 % aluminium-nickel alloy, according to the procedure described by Pavlic and Adkins (61). It was added to the crude mercaptal by means of 300 ml of 95 % ethanol, and the mixture was refluxed

Table 3

Fraction no.	Volume of eluent (ml)	Solvent	Weight of the eluated product (mg)	n_D^{25}
1	200	Light petroleum (b.p. 30–50°)	148	
2	100	Light petroleum	496	1.4490
3	100	Light petroleum	289	1.4489
4	100	Light petroleum	170	1.4489
5	100	Light petroleum	150	1.4490
6	100	Light petroleum	103	1.4487
7	300	Light petroleum	215	1.4485
8	200	Light petroleum–benzene 19:1	190	
9	200	9:1	285	1.4490
10	200	8:2	302	1.4492
11	200	1:1	109	1.4490
12	200	Benzene	5	
13	200	Benzene–ether 19:1	14	
14	200	9:1	7	
15	200	1:1	19	
16	300	Ether	24	
17	300	Ether–acetic acid 0.5 %	17	
Total			2543	

for 8 hours. The nickel was filtered off, and thoroughly washed with hot ethanol. The filtrate and washings were combined and evaporated to dryness *in vacuo*. The residue, a colourless oil, weighed 5.5 g.

3.5 g of the crude reduction product was chromatographed on 110 g of alumina (Merck, previously neutralized by means of nitric acid), see Table 3.

Fractions 2 to 5 were combined and distilled. The distillate was a colourless oil, b.p. 195–200° (temperature of the air bath), 0.3 mm. The distillate solidified on cooling and melted at 18.3–18.8°. $n_D^{23.5}$ 1.4496. $d_4^{23.5}$ 0.857.

R_D Calcd. for $C_{26}H_{52}O_2$ (396.7): 123.93
Found 124.25

Fractions 8 to 11 had b.p. 195–200° (temperature of the air bath), 0.3 mm, $n_D^{21.5}$ 1.4500 and $d_4^{21.5}$ 0.858.

R_D found 124.22

The first eleven fractions of the chromatography (2.457 g) were thus methyl *erythro*-3,5-dimethyltricosanoate. The yield in this reduction procedure was 64 %.

Saponification of this ester (2.06 g) gave 2.01 g of acidic fraction. Crystallization of *erythro*-3,5-dimethyltricosanoic acid from the crude molten product began by the low-melting form, and white balls of crystals of the high-melting form grew slowly on this solid product. After one crystallization from acetone (with addition of several drops of water), the melting point was 43.5–46° (Kofler).

erythro-3,5-Dimethyl-7-oxooctanoic acid (VI)**(a) Preparation through malonic ester synthesis**

The magnesium derivative of ethyl malonate was prepared by Bowman's method (62), from 24 g of ethyl malonate and 3.6 g of magnesium turnings. To the solution of ethyl ethoxy-magnesium-malonate, the acid chloride (prepared from 20 g of methyl hydrogen *erythro*-3,5-dimethylpimelate (I) by means of oxalyl chloride) was added under the conditions set out by Bowman (62).

The solution was hydrolyzed by addition of crushed ice and aqueous 10 % sulphuric acid, and the organic product isolated by extraction with ether. Excess of ethyl malonate was removed by distillation through a spiral column in vacuo (3 mm).

Acidolysis of the crude product was performed as described by Bowman (62) by heating under reflux with 80 g of propionic acid and 0.5 ml of concentrated sulphuric acid for 3 hours. To the cooled solution was added 7 ml of *N* sulphuric acid and the mixture refluxed for 1 hour more. After cooling, the solution was washed twice with water, and then diluted with ether (about 300 ml) and washed a further five times with water. A considerable loss of product was observed during this step owing to solubilization in the aqueous propionic acid layer. After drying the solution over sodium sulphate and evaporation of the solvents, only 15 g of product was recovered.

The crude product was distilled in a flask fitted with a short column (20 cm, filled with Wilson spirals):

	Weight	n_D^{25}
Fraction 1, collected at about 50°/16–17 mm	1.55 g	
2, from 120 to 130°/2 mm	2.0	1.4338
3, 130 to 140°/2 mm	3.49	1.4370
4, 154 to 160°/2 mm	1.46	1.4432
5, 160 to 163°/2 mm	4.57	1.4477

Fractions 2 and 3 gave a positive reaction with an alcoholic solution of ferric chloride, showing that some β -oxo-ester was still present and that acidolysis was incomplete.

Fractions 2 to 4 were then combined and saponified by heating under reflux with a solution of 7 g of sodium hydroxide in 100 ml of ethanol and 25 ml of water for 45 minutes. The acidic fraction was separated by means of the P reagent of Girard and Sandulesco (64) into a ketonic fraction (7.4 g) and a non-ketonic fraction (2.3 g). The latter fraction still contained some ketonic product as shown by a positive Legal test (65), probably due to a slight hydrolysis of the hydrazone of the Girard P reagent during the time required for breaking the emulsions.

Distillation of the ketonic fraction gave pure *erythro*-3,5-dimethyl-7-oxooctanoic acid (6 g, *i.e.* 32 % of yield) (VI), in the form of a colourless oil, of b.p. 160° (temperature of the air bath), 0.3 mm, n_D^{22} 1.4494, and d_4^{22} 0.9988.

<i>Anal.</i> : Calcd. for $C_{10}H_{18}O_3$ (186.2)	C, 64.48; H, 9.74 %
Found	C, 64.33; H, 9.90
R_D Calcd.	50.05
Found	49.92

(b) Preparation through reaction with methyl cadmium

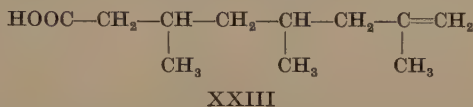
Methyl magnesium iodide was prepared in the usual way from 35 g of methyl iodide and 5.95 g of magnesium turnings. To the solution of the Grignard reagent, 24.5 g

of powdered dry cadmium chloride was added, and the mixture heated under reflux, while stirring constantly, for 75 minutes (32, 63). The complete transformation of the Grignard reagent into the cadmium derivative was not checked.

A solution of the acid chloride (prepared from 25 g of methyl hydrogen *meso*-3,5-dimethylpimelate (I) by means of oxalyl chloride) in 25 ml of dry benzene was slowly added to the well-stirred cadmium reagent. A very vigorous reaction took place during the first part of the addition, and the product in the flask became stickier and stickier. When all the acid chloride was added, the mixture was heated under reflux for 1 hour.

After treatment of the product of the reaction in the usual way (63), 30 g of a neutral, slightly yellow oil was obtained, which gave 20.5 g of a fraction distilling at 135°, 15 mm. This product was saponified by heating under reflux in a solution of 11 g of potassium hydroxide in 100 ml of aqueous ethanol (1:1 v/v) for 45 minutes giving 19 g of an acidic fraction.

Preliminary experiments showed that this acidic fraction was a mixture of the expected keto-acid (VI) and the unsaturated acid (XXIII), the formation of which



was probably due to reaction of methyl magnesium iodide, still present in our preparation of methyl cadmium, with the acid chloride, giving a tertiary hydroxy-ester that was dehydrated during distillation. Pure *erythro*-3,5-dimethyl-7-oxoöctanoic acid (VI) (4.1 g) was obtained from this mixture of acids (9.0 g) by separation by means of the T reagent of Girard and Sandulesco (64). The pure oxo-acid distilled at 160° (temperature of the air bath), 0.4 mm, and had n_D^{24} 1.4488.

Anal.: Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_3$ (186.2) C, 64.48; H, 9.74 %
Found C, 64.1; H, 9.6

erythro-4,6-Dimethyltetracosanone-2 (IV)

(a) Preparation through malonic ester synthesis

Ethyl ethoxy-magnesium-malonate was prepared according to the procedure described by Bowman (62) from 0.45 g of magnesium and 3 g of ethyl malonate. The acid chloride, prepared in the usual manner from 4.3 g of *erythro*-3,5-dimethyltricosanoic acid by means of oxalyl chloride, was added to the solution of ethyl ethoxy-magnesium-malonate in benzene. The mixture was heated under reflux for half an hour.

After cooling, the product of the reaction was hydrolyzed with ice and dilute (1:10 w/v) sulphuric acid, and extracted with ether. The crude product, obtained by evaporation of the ether extracts, was saponified by heating for 1 hour in a solution of 2.5 g of potassium hydroxide in 150 ml of 95 % ethanol. Extraction of the saponified product with ether gave 3.7 g of a neutral fraction and 0.5 g of an acidic fraction.

The neutral fraction was chromatographed on 120 g of alumina (Merck, neutralized). Elutions with light petroleum (b.p. 30–50°) gave 0.7 g of ethyl *erythro*-3,5-dimethyltricosanoate, in the form of a colourless liquid, m.p. 14.8–15.3°, b.p. 195–200° (temperature of the air bath), 0.3 mm, n_D^{22} 1.4495 and d_4^{22} 0.854.

R_D Calcd. for $C_{27}H_{54}O_2$ (410.7)	128.83
Found	129.07

This ester probably escaped saponification because of the mild conditions.

Elutions with a mixture of light petroleum and benzene (20 to 50 %) gave *erythro*-4,6-dimethyltetracosanone-2 (2.6 g, i.e. a yield of 60 % of the theoretical). This ketone had b.p. 190–195° (temperature of the air bath), 0.1 mm, and n_D^{25} 1.4515. It was identified by comparison with samples obtained through different procedures (see below).

(b) Preparation through methyl cadmium synthesis

Methyl magnesium iodide was prepared in the usual way from 0.72 g of magnesium turnings, 2 ml of methyl iodide, and 12 ml of ether. To the Grignard reagent 3 g of anhydrous, finely powdered cadmium chloride was added in one portion, and the mixture was heated under reflux, stirring constantly, for 2 hours (32, 63).

After cooling to room temperature, a solution of the acid chloride of *erythro*-3,5-dimethyltricosanoic acid (III) (prepared by means of oxalyl chloride from 4.3 g of the free acid) in 10 ml of dry benzene was slowly added to the stirred mixture, and the reaction was completed by heating under reflux for 1 hour.

The neutral product of the reaction (4.1 g), isolated in the usual way (63), was purified by chromatography on 120 g of alumina (Merck, neutralized), using elutions of 200 ml of solvent—see Table 4.

Fractions 1+2 could not be distilled at 250°/0.05 mm.

Fractions 4 to 13 were combined and distilled. *erythro*-4,6-Dimethyltetracosanone-2 (IV) was obtained in the form of a colourless liquid, b.p. 190–195° (temperature of the air bath), 0.1 mm, which solidified on cooling and melted at 20.9–21.4°.

Table 4

Fraction no.	Solvent	Weight of eluted product (mg)	n_D^{25}
1	Light petroleum (b.p. 30–50°)	38	
2	Light petroleum	138	1.4665
3	Light petroleum	485	1.4593
4	Light petroleum–benzene 9 : 1	800	1.4516
5	9 : 1	641	1.4518
6	9 : 1	265	1.4517
7	8 : 2	270	1.4518
8	8 : 2	285	1.4518
9	8 : 2	179	1.4518
10	7 : 3	160	1.4516
11	1 : 1	132	1.4518
12	1 : 1	81	1.4517
13	1 : 1	44	
14	Benzene	8	
15	Benzene–ether	1 : 1 352	
		Total	3878

Anal.: Calcd. for $C_{26}H_{52}O$ (380.7) C, 82.03; H, 13.77 %
 Found C, 82.12; H, 13.55

About 100 mg more was obtained from a second chromatography of fraction 3, so that a total amount of 2.95 g of ketone were obtained (i.e. a yield of 68.5%).

A *semicarbazone* was prepared, which, after crystallization from a mixture of ethanol and ether 2:1, melted at 82–83° (Kofler).

Anal.: Calcd. for $C_{27}H_{55}ON_3$ (437.9) N, 9.60 %
 Found N, 9.49
 9.46

Distillation of fraction 15 gave *erythro*-2,4,6-trimethyltetracosanol-2 (b.p. 190–195° (temperature of the air bath, 0.1 mm). The melting point of the product solidified by cooling was 24.0–24.6°. n_D^{25} 1.4555, and d_4^{25} 0.840.

Anal.: Calcd. for $C_{27}H_{56}O$ (396.7) C, 81.74; H, 14.23 %
 Found C, 81.4; H, 14.1
 81.4 14.2

(c) *Preparation through mixed electrolysis of stearic and erythro-3,5-dimethyl-7-oxooctanoic acids*

To a solution of 12 g of pure stearic acid (m.p. 69.4–69.6°) in 100 ml of absolute ethanol and 100 ml of methanol was added a solution of 0.1 g of sodium in 30 ml of methanol, followed by 4.0 g of pure *erythro*-3,5-dimethyl-7-oxooctanoic acid dissolved in 30 ml of methanol. 40 ml of methanol were used for rinsing.

Electrolysis was carried out with five platinum electrodes (60 × 50 × 0.1 mm) (two anodes) inserted into a bakelite frame (66), using a current of about 3 amps. The electrolysis was continued until the solution became neutral (about 1 hour). No external cooling was used (apart from a round flask filled with ether placed on top of the beaker to prevent excessive evaporation).

After cooling the solid products (mainly *n*-tetratriacontane) were filtered off and the solution concentrated in vacuo. The residues obtained from two such runs were extracted with light petroleum (b.p. 40–60°). These extracts were filtered, dried over

Table 5

I	20 to 105°/0.5 mm	0.293 mg	$n_D^{22.5}$
II	105–112°	0.360	1.4393
III	112–113°	0.987	1.4396
IV	113–115°	0.952	1.4396
V	115–120°	0.248	
VI	120–145°	0.713	Partly crystallized
VII	145–178°	0.994	Crystallized
VIII	178–180°	1.142	Crystallized
IX	180–181°	0.979	Crystallized
X	181–185°	1.127	Crystallized
XI	185–190°	1.055	Almost completely liquid
XII	190–193°	1.076	Liquid, $n_D^{21} = 1.4537$

Table 6

		mg	n_D^{25}
1	100 ml light petroleum	94	1.4532
2	100 ml light petroleum	227	1.4516
3	100 ml light petroleum-benzene 9:1	370	1.4517
4	8:2	475	1.4513
5	8:2	259	1.4514
6	5:5	225	1.4516
7	5:5	127	1.4513
8	300 ml ether	64	1.4521

sodium sulphate, and evaporated. 12 g of residue were thus obtained and distilled in a 50 ml Claisen type flask (Table 5).

Fractions XI and XII were chromatographed on a column of 65 g of alumina (Merck, previously neutralized) (Table 6).

Fractions 2-7 consisted of the expected *3,5-dimethyltetracosanone-2*.

This product distilled at 190-195° (temperature of air bath), 0.1 mm, and had n_D^{20} 1.4530, n_D^{25} 1.4514, and d_4^{20} 0.846.

Anal.: Calcd. for $C_{26}H_{52}O$ (380.7) C, 82.03; H, 13.77 %

Found C, 82.0; H, 13.6

R_D Calcd. 121.28

Found 121.56

Only 1.68 g of methyl ketone was obtained (yield 10.5 %).

Fractions III and VI from the above distillation were chromatographed on a column of 65 g of alumina (Merck, neutralized) (Table 7).

Fraction 1 distilled at 115-120° (temperature of the air bath), 0.5 mm, and had n_D^{24} = 1.4380 and d_4^{24} 0.7785. After solidification by cooling, it melted at 16.3-18.8°. This product was identified as a mixture of *n*-heptadecane and 1-heptadecene, arising during electrolysis through decarboxylation of discharged stearate ions (see ref. 67).

Table 7

		mg	n_D^{25}
1	100 ml light petroleum (b.p. 30-50°)	1364 (70.5 %)	
2	100 ml light petroleum	10	
3	100 ml light petroleum	0	
4	100 ml light petroleum-benzene 8:2	7	
5	1:1	43	1.4399
6	Benzene	3	
7	Benzene-ether 9:1	8	
8	8:2	101	1.4563
9	1:1	32	1.4561
10	150 ml ether	5	
11	ether-methanol 8:2	8	
12	ether-acetic acid 0.5 %	221	1.4476

<i>Anal.</i> : Calcd. for $C_{17}H_{34}$ (238.4)	C, 85.63; H, 14.37 %
Found	C, 85.7; H, 13.9
R_D Calcd.	80.24
Found	80.35

Perphthalic acid oxidation in ether solution showed an uptake of oxygen corresponding to 73 % of the theoretical, after 70 hours at room temperature.

Schmidt *et al.* (68) give the following constants for 1-heptadecene: b.p. 157°, 0.1 mm, m.p. 11°, n_D^{20} 1.4438, and d_4^{20} 0.7854.

2,4,6-Trimethyl-2-hydroxytetracosanoic acid (VIII)

(mixture of diastereoisomers)

To a solution of 6.8 g of pure *erythro*-4,6-dimethyltetracosanone-2 (IV) in 50 ml of dry ethanol, 0.5 ml of triethylamine and 20 ml of a mixture of ethanol and anhydrous hydrocyanic acid (1:1, v/v) were added. The mixture was left at room temperature for 18 hours.

After addition of 0.7 ml of concentrated hydrochloric acid, the mixture was evaporated to dryness *in vacuo*. A solid residue was obtained, which was placed in an exsiccator over potassium hydroxide *in vacuo* for 48 hours. The crude cyanohydrin thus prepared gave a strong positive test for nitrogen (according to Lassaigne). No attempt at purification was made.

Hydrolysis of the crude cyanohydrin was performed by heating 1.875 g of the product in a mixture of 120 ml of acetic acid and 65 ml of concentrated hydrochloric acid on a boiling water bath for 3 hours. 50 ml of acetic acid was then added, and the solution (not completely homogeneous) was heated under reflux for a further 25 hours. A current of dry gaseous hydrogen chloride was passed through the solution during 10 minutes after 5, 9 and 21 hours of refluxing. After cooling, about 50 ml of water was added, and the almost white, solid product which precipitated was collected by filtration. This product was dissolved in ether and the ether solution washed with 5 % aqueous potassium hydroxide. A neutral and an acidic fraction were obtained, the latter being the expected α -hydroxy-acid (VIII). Four such runs were performed (Table 8).

From 6.8 g of *erythro*-4,6-dimethyltetracosanone-2, a total amount of 2.85 g of crude 2,4,6-trimethyl-2-hydroxytetracosanoic acid (VIII), m.p. 48–51° (Kofler), was obtained (i.e. a yield of 36 %). Chromatography on alumina of the neutral fraction showed that it contained a large amount of 4,6-dimethyltetracosanone-2 (IV).

A sample of 2,4,6-trimethyl-2-hydroxytetracosanoic acid (VIII) was purified by

Table 8

Experiment	Weight of material, g			
	1	2	3	4
Crude cyanohydrin	1.875	1.936	1.805	2.220
Neutral fraction	0.810	1.044	1.153	1.350
Acidic fraction	0.890	0.685	0.530	0.740

Table 9

Fraction no.	Solvent	Weight of product eluted, mg
1	Light petroleum (b.p. 30–50°)	3
2	Light petroleum–benzene 9:1	0
3	1:1	42
4	1:1	41
5	1:1	15
6	Benzene	3
7	Benzene–ether 98:2	1
8	Ether	2
Total		107

chromatography of its methyl ester (prepared by means of diazomethane). 118 mg of crude ester was chromatographed on 4 g of alumina (Merck, neutralized and slightly de-activated), using elutions of 10 ml of solvent (Table 9).

Distillation of the combined fractions 3, 4, and 5 gave pure methyl 2,4,6-trimethyl-2-hydroxytetracosanoate in the form of a white crystalline product that had m.p. 22.5–23.1°, b.p. 170–180° (temperature of the air bath), 0.3 mm, and n_D^{25} 1.4527. The ultraviolet spectrum showed no prominent absorption between 206 and 310 $m\mu$. The infrared spectrum (Fig. 5*b*) showed bands at 2.85 μ (OH group) and 5.77 μ (ester group).

Anal.: Calcd. for $C_{28}H_{56}O_2$ (440.7) C, 76.30; H, 12.81 %
 Found C, 76.74; H, 12.83

erythro-2,4,6-trimethyltetracos-2-enoic acid (IX)

1.15 g of 2,4,6-trimethyl-2-hydroxytetracosanoic acid was heated in a small flask at 207–208° (internal temp.) for 1 hour and at 212–215° for half an hour. Care was taken not to heat beyond this point, since it has been shown (21, 37) that the lower the temperature of pyrolysis, the greater the yield of *cis*-compound.

After cooling, the brownish liquid was dissolved in a few ml of ether, and an excess of a solution of diazomethane in ether was added. After half an hour, the solution was evaporated *in vacuo* and dried in an exsiccator. The crude product had $\lambda_{\max}$ 216 $m\mu$, and $\epsilon_{\max}$ = about 6,000.

The product obtained from two such runs (about 2.4 g of crude ester) was chromatographed on 200 g of alumina (Merck, neutralized, slightly de-activated with 2 ml of water) (column, internal diameter 20 mm, height of alumina 520 mm) (Table 10).

Fractions 5–13 contained essentially the *cis*-isomer of the $\alpha\beta$ -unsaturated ester, and fractions 23–34, the *trans*-isomer. Each group of fractions was chromatographed again (see below). Fractions 17 and 18 contained mainly the α -methylene isomer, as shown by the ultraviolet absorption maximum. Owing to the small amount of material no attempt at further purification was made. Fractions 40 to 50 contained essentially 4,6-dimethyltetracosanone-2, to judge from the place of elution and the refraction index. Lucas and Prater (37) observed that some methyl ketone can be recovered from pyrolysis mixtures of this type.

Table 10

Fraction no.	Volume of eluent (ml)	Solvent	Weight of product eluated (mg)	n_D^{25}	$\lambda_{\max}$ (m μ)	ϵ
1	100	Light petroleum (b.p. 30–50°)	1			
2	50	Light petroleum	17			
3	50	Light petroleum	1			
4	50	Light petroleum	2			
5	50	Light petroleum	66	1.4587		
6	50	Light petroleum	94	1.4585		
7	50	Light petroleum	95	1.4582	218	9.350
8	50	Light petroleum	84	1.4582		
9	50	Light petroleum	82	1.4582		
10	50	Light petroleum	49	1.4581		
11	50	Light petroleum	47	1.4581		
12	50	Light petroleum	30	1.4581		
13	50	Light petroleum	23	1.4580		
14	50	Light petroleum	21	1.4575		
15	50	Light petroleum	17			
16	50	Light petroleum	15	1.4563		
17	50	Light petroleum	15			
18	50	Light petroleum	19	1.4558	207.5	7.310
19	50	Light petroleum	38	1.4568		
20	50	Light petroleum				
21	50	Light petroleum				
22	50	Light petroleum	44	1.4571		
23	50	Light petroleum	49	1.4583		
24	50	Light petroleum				
25	50	Light petroleum				
26	50	Light petroleum	43	1.4591		
27	50	Light petroleum				
28	50	Light petroleum	40	1.4593	216	11.995
29	50	Light petroleum				
30	50	Light petroleum	32	1.4594		
31	50	Light petroleum				
32	50	Light petroleum	29	1.4597		
33	50	Light petroleum–benzene 99 : 1	19	1.4595		
34	50	99 : 1				
35	50	99 : 1				
36	50	99 : 1	19			
37	50	99 : 1				
38	50	99 : 1	23			
39	50	99 : 1				
40	50	99 : 1	7			
41	50	95 : 5				
42	50	95 : 5	11			
43	50	95 : 5				
44	50	95 : 5	11			
45	50	95 : 5				
46	50	95 : 5	11			
47	100	9 : 1	50	1.4520		
48	100	9 : 1				
49	100	1 : 1	213	1.4515		
50	100	1 : 1				
51	100	1 : 1	18	Solid		
52	100	1 : 1				
53	100	Benzene	12			
54	100	Benzene				
55	100	Benzene–ether 9 : 1	56	1.4675		
56	100	9 : 1		Viscous yellow oil		
57	500	Ether	277	1.4580		
				Mobile yellow oil		
58	500		17			
59	500	Ether–acetic acid 99 : 1	483	1.4618	217 6260	
				Slightly brown solid		
Total			2179			

Fraction 59 contained free acids, which had arisen either because of saponification of esters on alumina during the chromatography, or by the presence of some acidic fraction less easily esterified. The ultraviolet spectrum shows that it contains $\alpha\beta$ -unsaturated acids.

Cis-fraction

Fractions 5 to 13 were combined (crystallized product, m.p. 32–34° (Kofler)), and chromatographed on 60 g of alumina (same batch as the one used in the former chromatograms). The alumina column had an internal diameter of 14 mm and a height of adsorbant of 450 mm. (Table 11.)

The second fraction distilled at 180–190° (temperature of the air bath), 0.1 mm. The distillate rapidly crystallized giving a form which melted at 35.2–36.6°. After rapid cooling of the melt, the solidified product melted at 16.3–16.6°.

Anal.: Calcd. for $C_{28}H_{54}O_2$ (422.7) C, 79.55; H, 12.88 %
Found C, 79.28; H, 12.55

125 mg of *cis*-ester were saponified by heating for 4 hours under reflux in a solution of 100 mg of potassium hydroxide in 5 ml of methanol and 2 ml of benzene. After crystallization from light petroleum, the acid melted at 66.9–68.0°.

Trans-fraction

Fractions 23 to 32 of the first chromatogram were combined and chromatographed again on 30 g of alumina (Merek, same quality). The column had an internal diameter of 8 mm, and the height of adsorbant was 480 mm. (Table 12.)

Distillation of fractions 17 to 23 gave *trans* methyl ester in the form of a colourless oil, b.p. 190–200° (temperature of the air bath), 0.1 mm, m.p. 14.3–14.7°, n_D^{25} 1.4600. Within about 15 days, another form crystallized, which melted at 30.5–31.5°.

Anal.: Calcd. for $C_{28}H_{54}O_2$ (422.7) C, 79.55; H, 12.88; (O)CH₃, 3.56 %
Found C, 79.35; H, 12.66; (O)CH₃, 3.53 %

Table 11

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)	n_D^{25}	λ_{max} (m μ)	ϵ
1	50	Light petroleum (b.p. 30–50°)	0			
2	30	Light petroleum	167	1.4587	217	10.236
3	20	Light petroleum	156	1.4583	217	9.730
4	20	Light petroleum	73	1.4582	216.5	8.808
5	20	Light petroleum	54	1.4582		
6	20	Light petroleum	37	1.4582		
7	20	Light petroleum	23	1.4581		
8	20	Light petroleum	23	1.4580		
9	20	Light petroleum	11	1.4578		
10	100	Light petroleum	24	1.4577		
Total			568			

Table 12

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)	n_D^{25}
1	50	Light petroleum (b.p. 30–50°)	0	
2	20	Light petroleum	0	
3–9	10	Light petroleum	0	
10	10	Light petroleum	3	
11	10	Light petroleum	7	1.4571
12	10	Light petroleum	9	1.4575
13	10	Light petroleum	7	
14	10	Light petroleum	9	1.4590
15	10	Light petroleum	8	
16	10	Light petroleum	7	1.4600
17	20	Light petroleum	15	1.4600
18	20	Light petroleum	11	1.4600
19	20	Light petroleum	12	1.4600
20	20	Light petroleum	15	1.4600
21	20	Light petroleum	14	1.4600
22	20	Light petroleum	13	1.4600
23	50	Light petroleum	32	1.4600
24	50	Light petroleum	15	1.4598
Total			177	

90 mg of the *trans*-ester were saponified by heating under reflux in a solution of 100 mg of potassium hydroxide in 5 ml of methanol and 2 ml of benzene for 4 hours. After crystallization from acetone, the *trans*-acid was obtained in the form of a crystalline powder which melted at 44.5–47.2°. After rapid cooling of the melt the solidified product melted at 22.4–23.1°.

Methyl erythro-3,5,7-trimethyl-7-acetoxyoctanoate (XI)

Methyl magnesium iodide was prepared in the usual way from 35 g of methyl iodide and 6 g of magnesium turnings in 125 ml of ether. The acid chloride prepared from 25 g (equimolecular amount) of methyl hydrogen *meso*-3,5-dimethylpimelate (I) (by means of oxalyl chloride) was dissolved in 250 ml of dry ether and cooled to –15°. To this solution, the ether solution of methyl magnesium iodide was added drop by drop stirring vigorously. The addition took about 40 minutes. The temperature at the end of addition was –5°. The mixture was then allowed to attain room temperature within half an hour, and stirring was continued for another half hour.

The mixture was then poured onto crushed ice and solid ammonium chloride was added to dissolve magnesium hydroxide. Organic material was extracted with ether. The ether solution was washed with a 1 % aqueous sodium hydroxide and with water until neutral, dried over sodium sulphate, and evaporated to dryness in vacuo. 25 g of neutral product (i.e. a yield of 93 %) was obtained, which gave a negative Legal test (65) (showing the absence of ketone).

Test for unsaturation showed the presence of only about 6 % of unsaturated material in the crude product thus obtained: 0.102 g of the crude hydroxy-ester required the addition of 0.50 ml of a 1 % solution of bromine in carbon tetrachloride to

give a stable colour. 8.2 ml of the same solution would have been required for the completely dehydrated product. Saponification of 0.5 g of the crude hydroxy-ester (X) by heating in a solution of 2 ml of aqueous sodium hydroxide (2 *N*) and 2 ml of ethanol for half an hour gave 0.435 g of acid (i.e. 94 % of the theoretical); only 0.014 g of unsaponifiable material was obtained, showing that the reaction with methyl magnesium iodide left the ester group of (I) unchanged. 0.205 g of the acid obtained from the saponification on titration consumed 9.8 ml of 0.1 *N* sodium hydroxide.

Anal.: Calcd. for $C_{11}H_{22}O_3$ M.W. 202.3

Found

209

An attempt to acetylate the crude hydroxy-ester (X) under the conditions described by Mills (69) was unsuccessful; almost all the product was recovered unchanged. This fact can be easily explained by the greater reactivity of the tertiary alcohols used by Mills (69) which were allylic. Heating of 2 g of the hydroxy-ester (X) in 20 ml of acetic anhydride at 100° for 2 hours was also ineffective.

Acetylation was finally performed by heating 20.4 g of the hydroxy-ester (X) (recovered from the previous attempts) in acetic anhydride under reflux for 3 hours. Acetic anhydride was removed by evaporation under reduced pressure (14 mm). The residue was dissolved in ether, and the solution was washed with a 1 % aqueous sodium hydroxide, and then with water until neutral, and subsequently dried over sodium sulphate and evaporated to dryness.

0.073 g of the crude acetoxy-ester (XI) thus obtained required 0.6 ml of a 1 % solution of bromine in carbone tetrachloride to give a stable colour. (The completely dehydrated ester would have required 5.90 ml of the bromine solution.) This shows that about 10 % of unsaturated ester is present in the crude acetoxyester.

The crude acetoxy-ester was distilled in a Claisen-type flask. (Table 13.)

Table 13

Fraction no.	Distillate collected at	Weight of the fractions (g)	n_D^{25}	d_4^{25}
1	83–85°, 0.2 mm	4.46	1.4355	0.955
2	92°, 0.2 mm	7.34	1.4358	0.965
3	92–94°, 0.2 mm	6.11	1.4358	0.965
4	94–100°, 0.2 mm	0.51	1.4360	

Fraction 1 is a mixture of the expected acetoxy-ester (XI) and the unsaturated ester.

Fractions 2 and 3 were combined giving 13.45 g of methyl *erythro*-3,5,7-trimethyl-7-acetoxyoctanoate (XI) (i.e. a yield of 51 % calculated on the half ester (I). Test for unsaturation was negative.

Anal.: Calcd. for $C_{14}H_{26}O_4$ (258.3) C, 65.08; H, 10.14 %

Found

C, 64.8; H, 10.0

R_D

Calcd.

70.16

Found

69.94

***erythro*-3,5,7-Trimethyl-7-acetoxyoctanoic acid (XII)**

A solution of 13.2 g of the acetoxy-ester (XI) in 15 ml of methanol containing a trace of phenolphthalein was warmed on a water bath at 70°. 19.8 ml of an aqueous solution of sodium hydroxide (2.5 *N*) (theoretical amount) was added in 4 portions. Each new addition was made only when the solution had been completely decolourized (this took about 15 minutes). 2.09 g of a neutral fraction and 10.3 g of an acidic fraction were obtained by extraction with ether.

The neutral fraction was dissolved in 2.5 ml of methanol and heated at 70° for half an hour after addition of 2 ml of a solution of 2.5 *N* sodium hydroxide. 1.10 g more of the acidic material was isolated.

The acidic fractions were combined, giving 11.4 g of *erythro*-3,5,7-trimethyl-7-acetoxyoctanoic acid (i.e. a yield of 90%). 0.193 g of this acid was heated under reflux for 1½ hour in 1 ml of aqueous sodium hydroxide (2.5 *N*). In the titration of the solution with 0.1 *N* aqueous sulphuric acid 15.2 ml of 0.1 *N* sodium hydroxide were consumed (the theoretical amount of sodium hydroxide 0.1 *N* to neutralize and saponify acetoxy-acid would have been 15.8 ml). The content of acetoxy group in our preparation of the acetoxyacid (XII) was thus at least 92 % of the theoretical.

***erythro*-3,5-Dimethyl-6-bromohexanoic acid (XV)**

The silver salt of methyl hydrogen *meso*-3,5-dimethyl pimelate (I) was prepared in the usual way (39, 70) from 30 g of half ester. 38 g of dry silver salt was obtained (i.e. a yield of 80 %).

This silver salt was dried at 100° in vacuo over P₂O₅ for 24 hours, and suspended in 60 ml of dry carbon tetrachloride. Dry bromine (about 12 ml) was added to the vigorously stirred suspension (39, 70), until the colour of the free bromine persisted. The mixture was then heated under reflux for 1 hour. The neutral product of the reaction, isolated in the usual way (39), weighed 23 g. It distilled, with a 25 cm column filled with Wilson pyrex glass helices, at 126–128°, 16 mm. 16 g of methyl *erythro*-3,5-dimethyl-6-bromohexanoate (XIV) was obtained (i.e. a yield of 62 %, calculated on the silver salt).

16 g of the bromo-ester (XIV) was heated under reflux in 50 ml of acetic acid and 4 ml of aqueous 40 % hydrobromic acid for 8 hours (39). The mixture was evaporated in vacuo and the residue dissolved in ether. The ether solution was extracted with aqueous 5 % sodium carbonate. The alkaline solution was acidified and extracted with ether. The acidic fraction was distilled in a Claisen-type flask, giving 9.6 g of *erythro*-3,5-dimethyl-6-bromohexanoic acid (XV) (i.e. a yield of 29 %, calculated on the half ester (I)), in the form of a colourless liquid, b.p. about 104°, 0.5 mm, n_D^{21} 1.4750 and d_4^{21} 1.298.

R_D Calcd. for C ₈ H ₁₅ O ₂ Br (223. 2)	48.44
Found	48.37

The neutral fraction (3.8 g) contained mainly *meso*-2,4-dimethyl-1,5-dibromopentane but no attempt to purify the products was made.

Calcd. for C ₇ H ₁₄ Br ₂	Br, 61.83 %
Found	Br, 59.37 %

erythro-2,4-Dimethyldocosanyl bromide (XVI)

To a solution of 11.5 g of stearic acid (m.p. 69.2–69.6°) in 100 ml of absolute ethanol and 150 ml of methanol, were added a solution of 0.1 g of sodium in 50 ml of methanol and 4.6 g of the bromo-acid (XV).

Mixed electrolysis was carried out as described above. After 45 minutes the solution became slightly alkaline and the current was immediately interrupted.

The alcoholic solutions obtained from two such runs were combined. After cooling, a solid product was filtered off and washed with light petroleum (b.p. 30–50°). The insoluble compound was almost pure *n*-tetratriacontane. (Crystallization from benzene gave shiny leaflets, m.p. 72.5–72.7°). The filtered solution and the light petroleum washings were combined and concentrated *in vacuo*. A large volume of light petroleum was then added. The light petroleum solution was washed with 10 % aqueous sulphuric acid, and then with water until neutral, dried by means of sodium sulphate, and evaporated to dryness. The residue was distilled using a 50 ml Claisen-type flask. (Table 14.)

Fractions 9 and 10 were combined and chromatographed on 60 g of alumina (Merck, neutralized) to remove any stearic acid still present. 1.4 g of pure *erythro-2,4-dimethyldocosanyl bromide* (XVI) was obtained from the first elutions with light petroleum in the form of a colourless liquid, b.p. about 200° (temperature of the air bath), 0.1 mm, n_D^{20} 1.4635 and d_4^{20} 0.950. This product, solidified by cooling, melted at 14.7–15.1°.

<i>Anal.</i> : Calcd. for $C_{24}H_{48}Br$ (417.5)		Br, 19.14 %
Found		Br, 18.87 %
R_D	Calcd.	120.99
	Found	120.91

Fractions 11 and 12 were combined and purified as described for fractions 9 and 10: 2.35 g of pure *erythro-2,4-dimethyldocosanyl bromide*, n_D^{20} 1.4635 was obtained. 3.75 g of the aliphatic bromide (XVI) was thus obtained, corresponding to a yield of 21 %, calculated on the 3,5-dimethyl-6-bromohexanoic acid (XV).

Table 14

Fraction no.	Product collected at (b.p., 0.5 mm)	Weight of the fractions (g)	n_D^{25}
1	80–114°	0.980	1.4482
2	114–115°	0.919	1.4426
3	115–118°	0.966	1.4445
4	119–210°	0.556	1.4495
5	125–130°	0.697	Partly crystal- lized
6	135–140°	0.797	"
7	170–182°	0.457	"
8	182–195°	0.934	"
9	195–203°	0.832	"
10	203°	1.067	"
11	203°	1.265	1.4642
12	203°	1.245	1.4640

erythro-2,4,6-Trimethyltetracosanol-2 (XVII)

3.75 g of *erythro*-2,4-dimethyldocosanyl bromide, 0.24 g of magnesium turnings (previously treated with methyl iodide in dry ether), 9 ml of *n*-dibutyl oxide, and one crystal of iodine were gently heated together under reflux (42). The beginning of the reaction was easily visible, but after 20 minutes the reaction stopped almost completely because of the precipitation of a heavy white product on the magnesium. Addition of 3 ml of dibutyl oxide was without result, but after 10 ml of diethyl oxide had been added the precipitate dissolved.

Titration of the magnesium derivative with iodine, as described by Job and Reich (75), showed that at least 10 % of the initial amount of dimethyldocosanyl bromide had been transformed into the Grignard reagent.

After addition of a trace of HgCl_2 , the mixture was heated under reflux for another hour. To the still warm mixture 2 ml of purified acetone were cautiously added: a vigorous reaction took place, with the formation of a heavy, sticky precipitate. After addition of 5 ml of dry benzene, the mixture was heated at 60° for 1 hour.

Hydrolysis was performed in the usual way by means of crushed ice, and ammonium chloride was added to dissolve magnesium hydroxide. After extraction with ether, the organic product, obtained in the form of a yellowish oil, was chromatographed on 90 g of alumina (Merck, neutralized) (Table 15).

Fraction 1 was separated by distillation in a small Claisen-type flask into subfractions (*a* and *b*).

(*a*) was collected at 160–170° (temperature of the air bath), 0.1 mm, about 2 g of a colourless liquid, n_D^{24} 1.4482, which appears to be slightly impure 2,4-dimethyldocosene ($\Delta^{1:2}$ or $\Delta^{2:3}$).

Anal.: Calcd. for $\text{C}_{24}\text{H}_{48}$ (336.6) C, 85.63; H, 14.37 %

Found C, 85.8; H, 14.7

(*b*) weighed 0.57 g and could not be distilled at 260° (temperature of the air bath), 0.1 mm, but distilled at 270°, 0.05 mm, in a simpler apparatus. It was a mixture of stereo-isomers of 19,21,24,26-tetramethyltetracontane which melted at 27.5–33.0°; after solidification of the melt by rapid cooling, it melted at 22.0–22.5°.

Table 15

Elution no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)
1	400	Light petroleum (b.p. 30–50°)	2675
2	200	Light petroleum	10
3	200	Light petroleum–benzene 75 : 25	29
4	200	1 : 1	0
5	200	Benzene	0
6	200	Benzene–ether 75 : 25	3
7	200	1 : 1	12
8	200	Ether	44
9	200	Ether	170
Total			2940

Anal.: Calcd. for $C_{48}H_{98}$ C, 85.37; H, 14.63 M.W. 675.2
 Found C, 84.86; H, 14.66 M.W. (Rast) 693, 708

Fractions 8 and 9 were combined. They distilled at 180–190° (temperature of the air bath), 0.1 mm, giving about 2.0 g of liquid *erythro-2,4,6-trimethyltetracosanol-2* (XVII) (i.e. a yield of 6 % of the theoretical), n_D^{25} 1.4560, which solidified slowly.

Anal.: Calcd. for $C_{27}H_{56}O$ (396.7) C, 81.74; H, 14.23 %
 Found C, 81.4; H, 14.2

After crystallizations from methanol and from 50 % aqueous acetone, the alcohol melted at 31.2–32.5°.

The same alcohol has been obtained as a by-product of the preparation of *erythro-4,6-dimethyltetracosanone-2* through methyl cadmium synthesis (see page 563).

erythro-2,4,6-Trimethyl-2-acetoxytetracosane (XVIII)

0.482 g of *erythro-2,4,6-trimethyltetracosanol-2* (XVII) was dissolved in 0.5 ml of dry xylene; 2 ml of acetic anhydride was added, and the mixture was heated under reflux for 2½ hours. After evaporation under reduced pressure (14 mm), the residue distilled at 180–200° (temperature of the air bath), 0.05 mm, giving 0.455 g (i.e. a yield of 84 % calculated on the free alcohol) of liquid *erythro-2,4,6-trimethyl-2-acetoxytetracosane* (XVIII), n_D^{23} 1.4498 and d_4^{23} 0.853. After solidification by cooling the product melted at 8.6–9.2°.

R_D Calcd. for $C_{29}H_{58}O_2$ (438.75) 138.02
 Found 137.78
Anal.: Calcd. for $C_{29}H_{58}O_2$ C, 79.38; H, 13.33 %
 Found C, 79.5; H, 13.3

erythro-2,4,6-Trimethyltetracosene-1 (XIII)

(a) *Mixed electrolysis of erythro-2,4,6-trimethyl-2-acetoxyoctanoic acid and stearic acid*

12.8 g of pure stearic acid (m.p. 69.4–69.6°) was dissolved in 100 ml of absolute ethanol and 200 ml of methanol. Solutions of 0.15 g of sodium in 50 ml of methanol, and of 5.5 g of *erythro-2,4,6-trimethyl-2-acetoxyoctanoic acid* (XII) in 50 ml of methanol, were added. Electrolysis was carried out as described above.

The alcoholic solutions obtained after two such runs were combined and treated as described above, to isolate the crude products of the coupling. 14 g of an oil was obtained, and this was distilled in a Claisen-type flask. (Table 16.)

Fractions 8 to 12 were combined (4.3 g) and chromatographed on 140 g of alumina (Merck, neutralized), using elutions with 300 ml of solvent. (Table 17.)

The combined *fractions 1 and 2* distilled at 190–200° (temperature of the air bath), 0.1 mm, giving about 2.5 g of *erythro-2,4,6-trimethyltetracosene-1* (XIII) (i.e. a yield of 13.4 % calculated on methyl hydrogen *meso-3,5-dimethylpimelate*). The unsaturated hydrocarbon was obtained in the form of a colourless liquid, n_D^{20} 1.4549 and d_4^{20} 0.811; the solidified product obtained by cooling melted at 10.2–10.6°.

Table 16

Fraction no.	Product collected at	Weight of the fractions (g)
1	58–100°, 1 mm	1.128
2	100°, 0.2 mm	1.033
3	100–110°, 0.2	1.050
4	110°, 0.2	0.961
5	110–140°, 0.2	1.218
6	140–142°, 0.2	1.211
7	142–170°, 0.2	1.147
8	170–182°, 0.2	1.166
9	182°, 0.2	1.032
10	176°, 0.1 mm	1.049
11	176°, 0.1	0.939
12	178°, 0.1	0.115

Table 17

Fraction no.	Solvent	Weight of eluated product (g)
1	Light petroleum (b.p. 30–50°)	2.450
2	Light petroleum	0.078
3	Light petroleum	0.053
4	Light petroleum–benzene 19 : 1	0.039
5	9 : 1	0.030
6	4 : 1	0.150
7	1 : 1	0.350
8	Benzene	0.280
9	Benzene	0.028
10	Benzene–ether 9 : 1	0.002
11	1 : 1	0.0
12	Ether	0.390
13	Ether	0.122
14	Ether	0.004
Total		3.948

Anal.: Calcd. for $C_{27}H_{54}$ (378.7) C, 85.63; H, 14.37 %

Found C, 85.7; H, 14.1

R_D Calcd. 126.42

Found 126.70

Fractions 6, 7, and 8 distilled at 190–200° (temperature of the air bath), 0.1 mm; the liquid obtained had n_D^{22} 1.4527 and d_4^{22} 0.839.

Anal.: Found C, 82.2; H, 13.4

C, 81.8; H, 13.8

It was obviously a mixture, and was not examined further.

Fractions 12 and 13 distilled at 200–210° (temperature of the air bath), 0.2 mm, giving about 0.5 g of *erythro*-2,4,6-trimethyltetracosanol-2 (XVII) (i.e. a yield of 2.8 % of the theoretical). The liquid alcohol had n_D^{24} 1.4554 and d_4^{24} 0.842. The solidified product obtained by cooling melted at 23.1–24.1°.

<i>Anal.</i> : Calcd. for $C_{27}H_{56}O$ (396.7)		C, 81.74;	H, 14.23 %
Found		C, 81.5;	H, 14.0
R_D	Calcd.	128.1	
	Found	128.4	

(b) *Pyrolysis of a mixture of erythro-2,4,6-trimethyl-2-acetoxytetracosane (XVIII) and stearic acid*

0.403 g of pure *DL-erythro*-2,4,6-trimethyl-2-acetoxytetracosane (XVIII) was mixed with 0.270 g of stearic acid in a small distillation apparatus. The temperature of the mixture was brought to 210° within 10 minutes, under a pressure of 10 mm. At that moment distillation began and was slowly continued until the temperature had risen to 230°. The distillate was chromatographed on 20 g of alumina to remove stearic acid. The first two light petroleum elutions (50 ml each) gave 0.30 g of *erythro*-2,4,6-trimethyltetracosene-1 (XIII) (i.e. a yield of 75 % of the theoretical), b.p. 170–180° (temperature of the air bath), 0.1 mm, n_D^{23} 1.4533 and d_4^{23} 0.808.

<i>Anal.</i> : Calcd. for $C_{27}H_{54}$ (378.7)		C, 85.63;	H, 14.37
Found		C, 85.8;	H, 14.2
		85.5	14.4
R_D	Calcd.	126.42	
	Found	126.73	

***erythro*-2,4,6-Trimethyl- $\Delta^{2:3}$ -tetracosenal-1 (XIX)**

(a) *Selenium dioxide oxidation of the hydrocarbon (XIII)*

0.870 g of *erythro*-2,4,6-trimethyltetracosene-1 (XIII) was dissolved in 10 ml of benzene, and 15 ml of acetic acid and 0.8 g of selenium dioxide were added. The mixture was heated under reflux for 7 hours. The solution was filtered, diluted with ether, and washed with 1 % aqueous sodium hydroxide and with water. After drying over sodium sulphate, the solvent was driven off. A dark yellow oil was obtained, which was dissolved in a small volume of ether. The ether solution was vigorously shaken with a drop of mercury (71) in order to destroy selenium complexes. A black insoluble powder precipitated and was filtered off. It was necessary to repeat this procedure seven times to remove selenium derivatives.

Finally, 0.760 g of a yellowish oil was obtained, which was chromatographed on 25 g of alumina (Merck, neutralized and slightly de-activated). 70 ml of solvent was used for each elution. (Table 18.)

Fraction 1 probably contained some unreacted hydrocarbon, because of the low ultraviolet absorption.

Fraction 2 contained almost pure *erythro*-2,4,6-trimethyl- $\Delta^{2:3}$ -tetracosenal-1 (XIX), which melted at 29.5–35° (Kofler). Heilmann *et al.* (72) give for an α,β -unsaturated α -branched aldehyde (2-ethyl- $\Delta^{2:3}$ -hexenal), λ_{max} 230 m μ , ϵ = 18.300 (in alcohol).

Table 18

Fraction no.	Solvent	Weight of eluated product (g)	$\lambda_{\max}$ (m μ)	ϵ
1	Light petroleum (b.p. 30–50°)	0.189	217	332
2	Light petroleum–benzene 1 : 1	0.197	225	15,547
3	Benzene	0.039		
4	Benzene–ether 1 : 1	0.095	220	7,400
5	Ether	0.072	215 (shoulder) (at 206.5)	3,960 4,170)
6	Ether	0.011		
7	Ether–acetic acid 99 : 1	0.038	217 (shoulder) (at 206)	3,820 5,180)
8	Ether–acetic acid 99 : 1	0.007		
		Total	0.648 g	

(b) *Via erythro-2,4,6-trimethyl- $\Delta^{2,3}$ -tetracosenol-1 (XXII)*

To a solution of 2 g of *erythro*-2,4,6-trimethyltetracosene-1 (XIII) in 8 ml of dry carbon tetrachloride, 1.04 g of N-bromosuccinimide (freshly crystallized from water; 10 % excess) was added. The mixture was heated under reflux for 4½ hours with an ordinary electric heater. Succinimide and unreacted N-bromosuccinimide were filtered off and washed with carbon tetrachloride. The filtrate and washings were combined and evaporated in vacuo. A sample of the residue was distilled. A mixture of stereo-isomers of 2,4,6-trimethyl-3-bromotetracosene-1 (XX) was obtained in the form of a slightly yellow oil, b.p. 180° (temperature of the air bath), 0.05 mm, n_D^{23} 1.4714.

Anal.: Calcd. for $C_{27}H_{53}Br$ (457.7) Br, 17.43 %
 Found Br, 17.5

The bulk of the bromo-derivative was used without further purification.

To a solution of 2.40 g of the crude bromo-compound (XX) in 40 ml of acetic acid and 10 ml of xylene were added 3.5 g of silver acetate and 0.5 ml of water. The mixture was heated under reflux for 2½ hours. Silver salts were filtered off and thoroughly washed with ether. The filtrate and the washings were combined, and the solvents distilled off. The residue (crude acetoxy-compound (XXI)) weighed 2.140 g. It was bromine-free and had no important ultraviolet absorption between 214 and 280 m μ . 2.13 g of the crude acetoxy-compound (XXI) was dissolved in 10 ml of dry ether and the solution added drop by drop to a solution of 1 g of lithium aluminium hydride in 50 ml of dry ether in a moisture-free apparatus. The mixture was left at room temperature for 1 hour, and the excess of $LiAlH_4$ was then destroyed by ethyl acetate added drop by drop. Crushed ice was added, and the mixture was shaken with 5 % aqueous sodium hydroxide. The organic material was extracted with ether. After the usual treatment, 1.99 g of a white solid was obtained.

Table 19

Fraction no.	Solvent	Weight of eluated product (g)
1	Light petroleum (b.p. 30–50°)	0.396
2	Light petroleum	0.165
3	Light petroleum	0.113
4	Light petroleum	0.076
5	Light petroleum	0.057
6	Light petroleum	0.045
7	Light petroleum–benzene 9 : 1	0.070
8	Benzene–ether 95 : 5	0.316
9	Ether	0.068
10	Ether	0.015
11	Ether–methanol 8 : 2	0.122
Total		1.443

1.46 g of the crude alcohol thus obtained was chromatographed on 30 g of alumina (Merck, neutralized and slightly deactivated), 100 ml of solvent being used for each elution. (Table 19.)

The most strongly adsorbed fractions (8 to 11) containing the expected unsaturated alcohol (XXII) were dissolved in 1.5 ml of dry pyridine. This solution was added to a fresh solution of 0.155 g of CrO_3 in 1.5 ml of dry pyridine (48). The mixture was left at room temperature for 21 hours. A solution of 0.100 g of sodium metabisulphite in 1 ml of water was then added, and the mixture was thoroughly stirred for about 10 minutes. After dilution with water, the aliphatic compounds were extracted with ether. The ether extracts were washed with water, with diluted sulphuric acid, and again with water, until neutral. The ether solution was dried on sodium sulphate, and the ether distilled off.

The residue (0.530 g) contained the expected $\alpha\beta$ -unsaturated aldehyde (XIX) as shown by the ultraviolet absorption curve (λ_{max} 225 m μ , $\epsilon = 7.280$) and the infrared absorption spectrum (characteristic bands at 3.72 μ and 5.92 μ , see above). It was used without further purification for the silver oxide oxidation experiments.

**Methyl erythro-2,4,6-trimethyl-*trans*- $\Delta^{2:3}$ -tetracosenoate (IX),
from the second route**

(a) From C_{27} aldehyde (XIX) obtained by SeO_2 oxidation

0.185 g of the $\alpha\beta$ -unsaturated aldehyde (XIX) was dissolved in 2.5 ml of *sec.* butanol and 1.5 ml of 95 % ethanol. A solution of 0.4 g of silver nitrate in 1 ml of water was then added.

The homogeneous solution was stirred with a magnetic stirrer, 3.5 ml of a solution of 1 N sodium hydroxide in 80 % ethanol was added in 3 portions, over a period of 12 hours, stirring throughout, at room temperature (73). The mixture was left overnight. On the following day a solution of 0.4 g of silver nitrate in 1 ml of water was added, along with 1 ml of *sec.* butanol and 1 ml of 95 % ethanol (to improve the solubility of long chain compounds in the reaction mixture). To the stirred mixture 3.5 ml of

Table 20

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)
1	15	Light petroleum (b.p. 30–50°)	0
2	15	Light petroleum–benzene 1:1	29
3	15	Benzene	72
4	15	Benzene	5
5	15	Benzene–ether 1:1	7
6	15	Ether	6
7	15	Ether	
8	45	Ether–acetic acid 99, 5:0.5	48
9	30	Ether–acetic acid 99:1	5
Total			172

a solution of 1 *N* sodium hydroxide in 80 % ethanol was added in 4 portions over a period of 6 hours.

The silver salts were filtered off and thoroughly washed with ethanol and ether. The combined filtrate and washings were diluted with water, acidified with diluted sulphuric acid and extracted with ether. The ether solution was washed with water, dried on sodium sulphate, and the ether distilled off. The residue weighed 0.184 g. It was chromatographed on 3.5 g of alumina (Prolabo (Paris)), neutralized and slightly de-activated)—Table 20.

The acidic fraction (no. 8) had $\lambda_{\max}$ 217 $m\mu$, $\epsilon = 11,000$. It was converted into methyl ester by means of diazomethane in ether solution. The crude ester was chromatographed on 12 g of alumina (Prolabo, same quality as before) (Table 21).

Fraction no 11 was distilled in a small, simple apparatus made of a pyrex glass tube. It distilled at 160–170° (temperature of the air bath), 0.2 mm. The liquid thus obtained had the properties of *trans*-isomer of methyl *erythro*-2,4,6-trimethyl- $\Delta^{2:3}$ -tetracosenoate: colourless liquid, n_D^{25} 1.4597, which solidified on cooling and remelted at 16.8–17.6°. The ultraviolet absorption spectrum showed a maximum at 217 $m\mu$ ($\epsilon = 11,900$). The infrared spectrum is shown in Fig. 1*d*.

Table 21

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)
1	15	Light petroleum	0
2	15	Light petroleum	0
3–6	15	Light petroleum	0
7–10	50	Light petroleum	0
11	50	Light petroleum–benzene 99:1	35
12	50	99:1	2
13	50	Ether	6
Total			43

(b) *From C₂₇-aldehyde obtained through the unsaturated alcohol (XXII)*

0.53 g of the crude $\alpha\beta$ -unsaturated aldehyde (XIX) was oxidized by means of silver oxide under the conditions described just above (73). The crude product (0.570) g was chromatographed on 12 g of alumina (Merck, neutralized and slightly de-activated) (Table 22).

The acidic fraction (No. 9) had $\lambda_{\max}$ 217 $m\mu$, $\epsilon = 8,600$. The methyl ester was prepared by means of diazomethane and the crude methyl ester chromatographed on 15 g of alumina (Merck, neutralized and slightly de-activated) (Table 23).

Fraction 2 had no absorption maximum in the ultraviolet between 214 and 285 $m\mu$. This fact, together with the weak adsorption, may be due to the saturated nature of this ester fraction.

Fraction 3 distilled at 160–170° (temperature of air bath), 0.1 mm. From the infrared spectrum this fraction appeared to be a mixture of saturated ester and *trans*-unsaturated ester.

Table 22

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)
1	25	Light petroleum	189
2	25	Light petroleum	31
3	25	Light petroleum-benzene 1:1	98
4	25	Benzene	66
5	25	Benzene-ether 9:1	16
6	25	1:1	29
7	25	Ether	2
8	25	Ether	9
9	50	Ether-acetic acid 99.2:0.8	95
			Total 535

Table 23

Fraction no.	Volume of eluent (ml)	Solvent	Weight of eluated product (mg)	n_D^{25}
1	25	Light petroleum	0	
2	10	Light petroleum	22	1.4561
3	5	Light petroleum	15	1.4578
4	5	Light petroleum	5	
5	5	Light petroleum	3	
6	10	Light petroleum	6	
7	10	Light petroleum	1	
8	50	Light petroleum	15	1.4598
9	50	Light petroleum	8	
10	50	Light petroleum	6	1.4595
11	50	Light petroleum	3	
12	50	Light petroleum	1	
			Total 85	

Fractions 8–10 that also distilled at 160–170°, 0.1 mm, had the properties of the *trans*-isomer of *erythro*-2,4,6-trimethyl- $\Delta^{2:3}$ -tetracosenoate. The colourless liquid of n_D^{25} 1.4598 solidified on cooling and remelted at 14.1–14.6°. The ultraviolet absorption had a maximum at 216 m μ (ϵ = 12.850). The infrared spectrum is reproduced in Fig. 1e.

SUMMARY

Methyl hydrogen *erythro*-3,5-dimethylpimelate (I) has been converted into *erythro*-4,6-dimethyltetracosanone-2 by lengthening of the chain either at the free carboxyl end via Bowman's malonic ester synthesis, or at the methyl ester end by conversion into *erythro*-3,5-dimethyl-7-oxooctanoic acid and Kolbe synthesis with stearic acid. The long chain ketone is converted into a mixture of the *cis* and *trans* isomers (together with some α -methylene compound) of *erythro*-2,4,6-trimethyltetracosen-2-oic acid by successive conversion into cyanohydrin, hydroxy-acid and $\alpha\beta$ -unsaturated acid (by pyrolysis of the hydroxy-acid). The isomeric acids are separated by chromatography of the methyl esters on alumina.

Alternative synthetic routes have been devised via *erythro*-2,4,6-trimethyltetracosene-1. The unsaturated hydrocarbon has been synthesized from (I) along two different routes and it has been converted into *erythro*-2,4,6-trimethyltetracosen-2-al-1 in two ways, (a) by direct oxidation with selenium oxide and (b) by successive conversion into *erythro*-2,4,6-trimethyl-3-bromotetracosene-1, *erythro*-2,4,6-trimethyltetracosen-2-ol-1 (allylic transposition) and oxidation of the unsaturated alcohol to aldehyde. The aldehyde, finally, on oxidation with silver oxide gives *trans*- $\alpha\beta$ -unsaturated acid.

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Kinetische Versuche an N-Oxyden

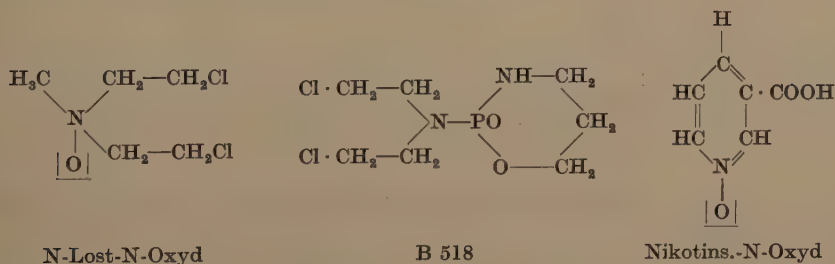
Von HANS v. EULER, HANS HASSELQUIST und OSKAR HEIDENBERGER

Mit 1 Figur im Text

Durch Einwirkung von Hydroperoxyd (oder anderen Peroxyden) auf gewisse, teils aliphatische, teils cyklische Stickstoff-Verbindungen entstehen Stoffe, die je N-Atom ein Sauerstoff-Atom mehr enthalten als das Ausgangsmaterial und die meist als N-Oxyde bezeichnet werden.

Mehrere dieser N-Oxyde sind von ausserordentlichem biochemischem und pharmakologischem Interesse. Besonders bemerkenswert ist, dass der sog. N-Lost und einige seiner Derivate unter den bis jetzt bekannten Stoffen die höchste Tumorerhemmende Wirkung und die grösste therapeutische Breite besitzt.

Das N-Lost, ferner dessen Derivat B 518 (Endoxan) und das Pyridin-Derivat Nikotinsäure-N-Oxyd (siehe hierzu G. R. Clemon u. H. Koenig, J. Chem. Soc. 1949, S. 231) werden folgendermassen formuliert:



Man weiss, besonders durch die eingehenden Arbeiten japanischer Forscher, E. Ochiai und seine Schule u. a. (1), dass das Verhalten der N-Gruppe der Pyridin-

und Chinolin-Abkömmlinge durch Substituenten im heterocyclischen Ring z. B. durch NO₂-Gruppen wesentlich beeinflusst wird. Auf die Untersuchungen von T. Yoshida, M. Ishidate, W. Nakahara, F. Fukuoka sowie von Druckrey, Schmähl und Preussmann, sowie von Brock und Arnold haben wir schon früher (2) hingewiesen.

In vorhergehenden Arbeiten haben wir (2) N-Oxyde der folgenden Verbindungen dargestellt:

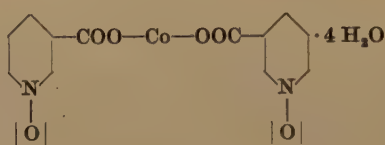
Cyklische Verbindungen: *Dimethyl-chinoxalin*. 7,8-Dimethyl-5-Nitro-chinolin¹; Pyridinderivate²; Nikotinsäure und Nikotinsäureamid; Isonikotinsäure; 5,6-Dimethylchinoxalin. Sulfathiazol; Phenanthrolin. Histidin und Riboflavin. Adenin.

In der vorliegenden Mitteilung wird zunächst das präparative Material ergänzt.

Nikotinsäure-N-oxyd-cobalt-salz. Während aus Nikotinsäureamid-N-oxyd keine Cobalt-Verbindung erhalten bzw. isoliert werden konnte — wir hatten die Bildung eines Chelates erwartet — entstand aus Nikotinsäure-N-oxyd in neutraler wässriger Lösung durch Zusatz von CoCl_2 das entsprechende Cobaltsalz.

Analyse:

Ber. für $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_6\text{Co} \cdot 4 \text{H}_2\text{O}$:	C 35,39 %	H 3,96 %	N 6,88 %	Co 14,47 %
Gef.	35,18	4,08	7,14	14,79



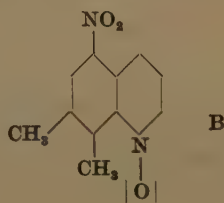
Im Anschluss an die von uns und von japanischen Forschern, besonders von E. Ochiai und Mitarb. beschriebenen Chinolin-N-Oxyde haben wir das *Akridin-N-Oxyd* dargestellt, und zwar durch Einwirkung von 5 ml Benzopersäure auf 0,5 g Akridin. Nach eintägigem Stehen bei Zimmertemperatur wurde die gelbbraune Lösung mit HCl-Lösung geschüttelt. Die salzsaure Schicht wurde alkalisiert und dann mit Benzol extrahiert. Aus der eingedunsteten benzolischen Lösung scheidet sich eine gelbe Kristallmasse ab, die nach Umkristallisieren kleine gelbe Nadeln vom Schmp. 153° lieferte.

Analyse (Subst. 297)

Ber. für $\text{C}_{13}\text{H}_9\text{ON} \cdot 2 \text{H}_2\text{O}$:	C 67,52 %	H 5,67 %	N 6,06 %
Gef.	68,40	5,90	6,25

Das N-Oxyd ist leicht löslich in Methanol, löslich in Benzol und Äthanol, unlöslich in Wasser.

¹ Wir nehmen für dieses Chinolin-N-Oxyd die Struktur B an:



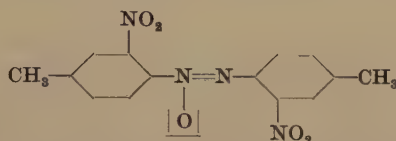
² Wir verdanken die Pyridin-Derivate der Freundlichkeit der Chem. Fabrik Dr. F. Raschig, GmbH, Ludwigshafen a. Rh.

Darstellung eines Azobenzol-N-Oxydes (Oxyazobenzols) aus 3-Nitro-4-amino-toluol und Hydroperoxyd

0,1 g 3-Nitro-4-amino-toluol in 10 ml Eisessig wurden mit 1 ml 30 %iger Perohydrolösung 24 Stunden bei 65° stehen gelassen. Nach dem Abkühlen kristallisierten kleine gelbe Stäbchen aus (Subst. 301).

Analyse Subst. 301

Ber. für $C_{14}H_{12}O_5N_4$: C 53,16 % H 3,83 % N 17,72 %
Gef. 52,41 3,89 17,14



Aus dem Filtrat schied sich nach einem weiteren Tag eine zweite Substanz, 303, in Form von hellgelben Stäbchen ab, die nach Umkristallisieren aus Methanol bei 58–59° schmolzen.

Beim Erwärmen mit dem Reduktionsmittel Ascorbinsäure gab die alkoholische Lösung von Subst. 303 eine vorübergehende rotviolette Farbe, wie sie für *o*-Dinitrobenzol (3) oder 3,4-dinitro-benzoesäure (4) charakteristisch ist.

Analyse Subst. 303

Berechnet für $C_7H_5O_4N_2$: C 46,16 % H 3,32 % N 15,38 %
Gef. 46,96 3,55 15,14

Die Subst. erweist sich also als 3,4-Dinitro-toluol, das somit aus dem entsprechenden 3-Nitro-4-amino-toluol durch Oxydation mittels H_2O_2 entstanden war. Der Befund, dass Hydroperoxyd imstande war, eine Aminogruppe zu einer Nitrogruppe zu oxydieren, beruht vielleicht auf der intermediären Bildung einer Hydroxylamingruppe.

Hydroperoxyd-Reaktion mit Biuret

Zwischen Biuret und Hydroperoxyd tritt schon bei Zimmertemperatur in wenigen Stunden ein Vorgang ein, bei dem sich aus der wässrigen Lösung lange rhombische farblose Kristalle ausscheiden. Dieselben wurden in einem Versuch mit Wasser und dann mit Petroleumäther gereinigt und schmolzen dann bei 152°. Sie waren in Petroleumäther und in Wasser schwer löslich, in Benzol und in Äthanol unlöslich.

Analyse Subst. 302.

Berechnet für $C_2H_5O_2N_3 \cdot 0,35 H_2O_2$: C 20,4 % H 5,0 % N 36,5 %
Gef. 21,4 5,7 35,5

6 Tage nach der Darstellung lag der Schmp. der Substanz 302 bei 201°. Nach 6maligem Umkristallisieren aus Wasser wurde *reines* Biuret vom Schmp. 200° erhalten, das keine Luminolreaktion gab.

Das Produkt 302 wurde in wenig Wasser gelöst und mit einer Lösung von 0,2 g KJ in 5 ml Wasser + 1 ml konc. HCl versetzt. Das ausgeschiedene Jod wurde mit einer Na-thiosulfatlösung titriert. Dabei zeigte sich, dass das Präparat 302 keiner konstanten Molekular-Verbindung entspricht. Das Produkt kann je nach den Versuchsbedingungen variieren.

Aus Biuret entsteht also durch Einwirkung von Hydroperoxyd *kein N-Oxyd*, sondern eine lockere Adsorptions-Verbindung, welche bei Zimmertemperatur ihr Hydroperoxyd wieder allmählich abspaltet.

Auch die Angaben von H. Stolzenberg (5) über seine Versuche mit Biuret, Alloxan und Allantoinensäure machen keine definierte Verbindung zwischen diesen Stoffen und Hydroperoxyd wahrscheinlich, noch weniger die Existenz von N-Oxyden.

Allgemeines Verhalten der N— $\overline{\text{O}}$ Gruppe

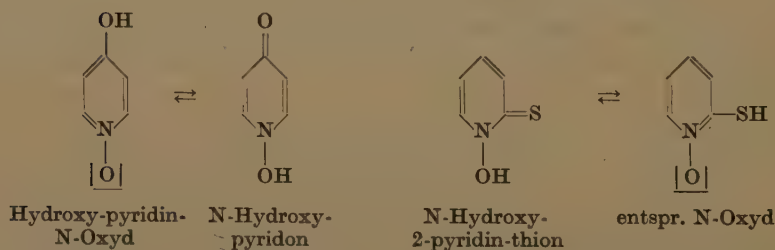
Da die Umsetzung, welche das N-Oxyd-Lost im Tierkörper beim Übergang in die „Wirkform“ erfährt, noch unvollständig aufgeklärt ist (vgl. S. 583), haben wir das Verhalten der N— $\overline{\text{O}}$ Gruppe der N-Oxyde an einfachen Fällen, zunächst an Nikotinsäure-N-Oxyd untersucht.

1. Acidität: Elektrometrische Messungen an der wässrigen Lösung von Nikotinsäure-N-Oxyd ergaben die gleichen pH-Werte wie Nikotinsäure.
2. Zinnchlorür in saurer Lösung reduziert.
3. Gegen starke Oxydationsmittel (Chromsäure) ist Nikotinsäure-N-Oxyd stabil.
4. Nach Ochiai (Vortrag, Mainz 1955) wird Pyridin-N-Oxyd leichter nitriert als Pyridin selbst.
5. Mit Aminen entstehen keine Schiffchen Basen.
6. In Eisessig ist Nikotinsäure-N-Oxyd stabil.

Eine Lösung von 344 mg N-Lost-N-Oxyd, HCl-Salz in 10 ml Eisessig bzw. 10 ml Wasser gelöst erwies sich bei den Aciditäten pH 2; 2,5; 5; 7,5; 8,5 vollständig stabil und zeigte keine Gasentwicklung.

7. *Mesomerien*: Zur Beurteilung der Elektronen-Verteilung in Hydroxy-N-Oxyden sei hingewiesen auf die (wahrscheinliche) Existenz der Gleichgewichte:

Hydroxy-pyridin-N-Oxyd $\rightleftharpoons$ N-Hydroxy-pyridon (6)
sowie N-Hydroxy-2-pyridin-thion mit der N-Oxyd-Form (8)



Zur Reaktionskinetik der Bildung von N-Oxyden

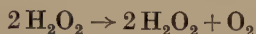
Substanz: $\text{H}_2\text{O}_2 = 3,75$ mmol, umgerechnet auf Gasvolumen = 84,0 ml C_0 .

Totale Lösungsmenge = 10 ml Eisessig.

Badtemperatur = $55^\circ\text{C} \pm 0,25$.

In diesem Versuch wurde die entwickelte O_2 volumetrisch gemessen.

Aus der einfachen Reaktionsformel:



ergibt sich: Für jedes Mol gebildeter O_2 zerfallen 2 Mol. H_2O_2 , also die zurückbleibende Menge H_2O_2 , in Gasvolumen ausgedrückt, zu jeder Zeit = $C_0 - 2 \times$ ml entwickelte O_2 . (Tab. 1.)

Tabelle 1.

Zeit in Min.	ml entwickelt O_2	ml Gasvol. H_2O_2	$C_0 - C$	$\ln \left(\frac{C_0}{C_0 - C} \right)$	$k \cdot 10^3$
0	0	0	84,0		
60	4,75	9,50	74,5	0,119	2,0
100	7,80	15,60	68,4	0,204	2,0
135	9,80	19,60	64,4	0,266	2,0
210	15,20	30,40	53,6	0,449	2,1
290	19,90	39,80	44,2	0,642	2,2
365	23,30	46,60	37,4	0,808	2,2

Wie der Versuch zeigt, spaltet sich H_2O_2 , berechnet auf die entwickelte O_2 , als Reaktion 1. Ordnung mit der Reaktionskonstanten

$$k = 2,1 \cdot 10^{-3}.$$

Substanz: $\text{H}_2\text{O}_2 = 5,05$ mmol.

Totale Lösungsmenge = 10,0 ml Eisessig.

Badtemperatur: $55^\circ\text{C} \pm 0,25^\circ$.

Wie Tab. 2 zeigt, ist die Zeit also direkt proportional mit den Logarithmen der Konzentrationen. H_2O_2 zerfällt in Eisessig als Reaktion 1. Ordnung.

Tabelle 2.

Zeit in t Min.	Verbrauch von 0,01 n. KMnO_4 in ml von 0,1 ml Probe	$\ln (C)$	$\frac{\ln C_1 - \ln C_2}{t_2 - t_1}$	Reaktions- konstanten $k \cdot 10^3$
0	10,20	2,32		2,0
40	9,35	2,24	$\frac{2,24 - 2,17}{75 - 40} = 2,0 \cdot 10^{-3}$	2,0
75	8,75	2,17	$\frac{2,17 - 2,02}{150 - 75} = 2,0 \cdot 10^{-3}$	2,0
150	7,55	2,02	$\frac{2,02 - 1,98}{175 - 150} = 1,6 \cdot 10^{-3}$	2,4
175	7,20	1,98	$\frac{1,98 - 1,89}{215 - 175} = 2,3 \cdot 10^{-3}$	2,0
215	6,60	1,89		

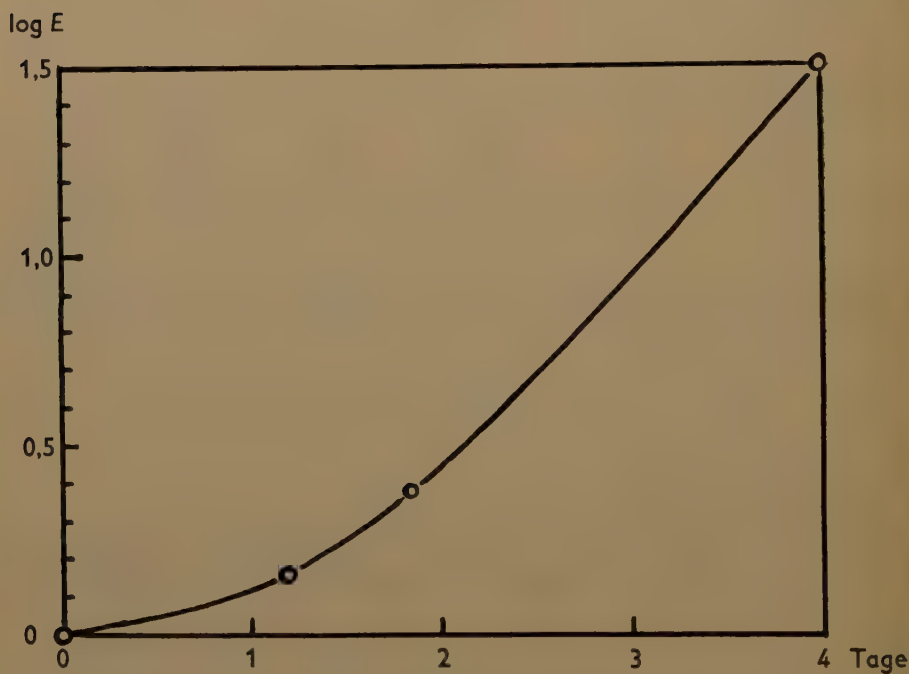


Fig. 1.

Zeitlicher Verlauf der Bildung von Nikotinsäure-N-Oxyd

Zur spektrometrischen Untersuchung (Fig. 1) im Beckman-Apparat wurden je 0,2 ml Wasser verdünnt und gemessen.

Die Reaktionslösung enthielt.

1,26 mmol Nikotinsäure }
10 mmol H₂O₂ } in 10 ml Eisessig.

Reaktionstemperatur: 23°.

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Tryckt den 8 april 1959

Uppsala 1959. Almqvist & Wiksells Boktryckeri AB

ERRATA

NILS-GÖSTA VANNERBERG, On the system $\text{SrO}_2\text{-H}_2\text{O-H}_2\text{O}_2$. 1. The crystal structure of α - and β - $\text{SrO}_2 \cdot 2\text{H}_2\text{O}_2$ (this volume, pp. 29—41).

In this paper the right coordination of Sr atoms has been missed. According to the structures of the compounds α - and β - $\text{SrO}_2 \cdot 2\text{H}_2\text{O}_2$ arrived at, the strontium ions are surrounded by one more oxygen tetrahedron than mentioned in the paper. The eight oxygen atoms then form a distorted dodecahedron.

The peroxide chains in the β -compound are linked into nets parallel with (100), which does not, either, follow clearly from the paper.

Corrections to be inserted

Page 34 Table 4 *add* Sr-O_1 $2.55 \pm 0.05 \text{ \AA}$
 $\text{Sr-O}_2'''$ 2.67 ± 0.08

Page 35 line 9 *for four read eight*
» 10 *for tetrahedron read dodecahedron*
» 10 *for 2.44 and 2.65 \AA read 2.44, 2.55, 2.65 and 2.67 \AA*

Page 39 line 7 *for double chains read nets*
Table 8 *add* $\text{Sr-O}_2'$ $2.69 \pm 0.07 \text{ \AA}$
 $\text{Sr-O}_1''''$ 2.79 ± 0.06

Page 40 line 16 *for tetrahedrally read dodecahedrally*
line 18 *for 2.38 and 2.56 \AA read 2.38, 2.56, 2.69 and 2.79 \AA*

